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Electron impact ionization of CH_3D and CD_4 near threshold: Isotope and temperature effects

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Abstract

Electron impact ionization near threshold was studied for the two isotopomers CH_3D and CD_4 using a high-resolution electron impact mass spectrometer. The appearance energies (AEs) of the parent and two fragment cations were determined for both molecules using a fitting procedure based on a modified Wannier type threshold power law. The present results are compared with the ionization thresholds for CH_4 studied previously with the same experimental setup. The deuterated molecules have always higher AEs than undeuterated CH_4. Moreover, for both molecules a downward shift in the AE was observed when the temperature was increased from 293 K to 693 K. The temperature effect measured on the AEs increases from CH_4 to CH_3D to CD_4.

Keywords: Methane; Deuterated; Ionization; Appearance energies

1. Introduction

The most recent high-resolution study on isotope effects of appearance energies (AEs) using electron impact ionization was carried out by Hanel et al. [1]. They investigated the isotopomers H_2/D_2, H_2O/D_2O and C_6H_6/C_6D_6 and compared the experimental results with standard quantum chemical calculations. They observed for all isotopomers upward shifts in the AE when going to the deuterated samples in the range of few tens of meV for the parent cation (of 40 meV for H_2O^+/H_2O and D_2O^+/D_2O) and up to a few hundred meV for the fragment cations (of 190 meV for H^+/H_2O and D^+/D_2O). Such a shift in the appearance energy for molecular isotopomers system can be expected due to the different molecular constants and moreover, due to different molecular potential energy curves for the different isotopomers.

The isotope effect on the appearance energy of methane was investigated for the first time around 1950 using electron impact ionization in combination with standard mass spectrometry [2,3]. Lossing et al. [2] carried out measurements for all five hydrogen/deuterium isotopomers of methane and observed that CH_3D has an AE of about 50 meV higher than CH_4. Moreover, in their article [3] they reported that the appearance energy of CD_4 is about 190 meV higher than the AE of CH_4. Besides electron impact experiments the isotope system CH_4/CD_4 has been also studied with other experimental techniques such as photoionization mass spectrometry (PI) [4–6] or photoelectron spectroscopy (PE) [7]. The most recent PI work by Berkowitz et al. [4] gave the value of the ionization energy for CD_4 about 40 meV higher than that of CH_4. They also reported quantum chemical calculations of the vibrational frequencies for CH_4 and CD_4 (und thus their zero point energies) and their respective cations. Based on these calculations a shift of 50 meV was predicted between the adiabatic ionization energies of CH_4 and CD_4, respectively. Thus, they assigned their experimentally observed shift exclusively to the difference in the zero point energies. Previous PI [5,6] and PE studies [7] reported, however, higher increases in the ionization energy between CH_4 and CD_4, i.e., between 80 meV and 180 meV.

All of these studies on methane concentrated mainly on the isotope effect for the parent cation. The threshold behavior of fragment cations of methane was much less investigated. Values

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for fragment cations were only reported by Dibeler et al. [5] (CH_3^+ and CH_2^+) using photoionization and Locht et al. [8] (H^+) using electron impact ionization.

We have carried out here high-resolution electron impact ionization experiments investigating the isotope effect for appearance energies of (partially) deuterated methanes (CH_3D and CD_4) and in addition we have investigated a possible temperature effect on the AEs with a temperature controlled molecular beam source. The threshold behavior of the electron impact ionization cross-section near the threshold for simple hydrocarbons was investigated at different gas temperatures and shifts in the AEs of up to 400 meV were observed [11–13].

In the present work we use the expression 'appearance energy (AE)' instead of IE (see exact definition in [13]) which is frequently used in previous literature, because we determine in the present experiment the minimum energy which is required to form the (fragment) cation from a neutral molecule in a vertical transition within the Franck Condon region (see also discussion in [12]).

2. Experimental setup

The apparatus used for the present measurements consists of a crossed electron/molecule beams setup in conjunction with a quadrupole mass spectrometer (see Fig. 1 for a schematic view). A more detailed description can be found in Ref. [14]. The neutral molecular beam is formed in an effusive molecular beam source (EMBS) which can be heated resistively up to 800 K. The gas samples of CH_3D and CD_4 were obtained from Sigma-Aldrich and have an isotope purity of 98% and 99%, respectively. For achieving a thermal equilibrium between the neutral gas and the heated walls of the beam source a deflector in the entrance of the beam source is mounted. This ensures that the molecules undergo a sufficient number of collisions before they effuse from the EMBS through a hole of 0.5 mm diameter. The neutral beam interacts in the collision region of a trochoidal electron monochromator (TEM) [15] with the monochromatized electron beam. The maximum electron energy resolution of the used TEM is about 30 meV, however the present measurements were carried out with an energy resolution of 120 meV leading to a higher detection sensitivity, i.e., the corresponding electron current at this energy resolution is about 50 nA.

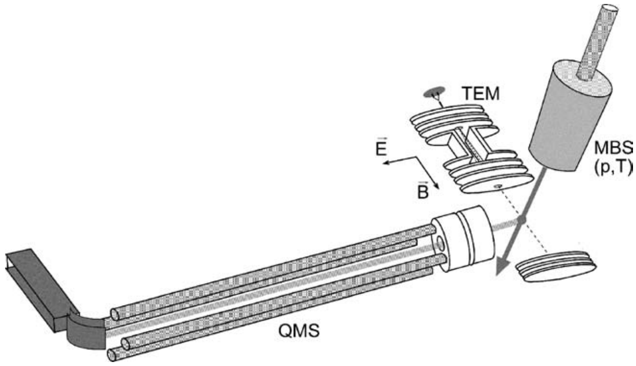

Fig. 1. Schematic view of the experimental setup. In the trochoidal electron monchromator (TEM) the monochromatized electron beam is formed. The electron beam interacts in the collision chamber with the neutral beam formed in the effusive molecular beam source (MBS). The ions formed are mass analyzed using a quadrupole mass spectrometer (QMS).

The ions formed in the collision region by the electron impact process are extracted into a quadrupole mass spectrometer (QMS) by a weak electric field and detected by a secondary electron multiplier (SEM) which is mounted off-axis. The SEM pulses are processed employing a pulse counting technique with computer. With this setup the ion efficiency curve for a mass-selected cation was measured as a function of the electron energy by repeatedly scanning the ramp voltage over a predefined energy interval near threshold. The electron energy scale of the monochromator was calibrated with the well known spectroscopic ionization energy of Ar^+/Ar (IE = 15.759 ± 0.001 eV) [16] by measuring the ionization efficiency curve of Ar under the same experimental conditions like those of the studied cations of CH_3D and CD_4.

For the exact determination of the appearance energy (AE) from the measured data a fitting method based on a modified Wannier threshold law [17] is used. Moreover, the fit function is constructed as a convolution of the electron energy distribution with the real cross-section. A detailed description and the reliability of the used fitting method is discussed in detail in Ref. [11] and [18]. In short, the measured ion efficiency curve is fitted with the following function $f(E)$ over the energy range that includes the threshold region:

$$f(E) = b \qquad \text{if } E < \mathrm{AE}_1 \tag{1a}$$

$$f(E) = b + c(E - \mathrm{AE}_1)^p \qquad \text{if } \mathrm{AE}_1 E < \mathrm{AE}_2 \tag{1b}$$

$$f(E) = b + c(E - \mathrm{AE}_1)^{p_1} + d(E - \mathrm{AE}_2)^{p_2} \quad \text{if } E > \mathrm{AE}_2 \tag{1c}$$

The fit using (1a) and (1b) involves four parameters: the background signal b, the unknown appearance energy AE_1, the scaling constant c which represents the slope of the cross-section above the AE_1 and the exponential factor p ("Wannier" factor). For a second threshold (designated as AE_2) in an ion efficiency curve where an energetically higher ionic state of the cation becomes accessible or another ion is present at this mass, the fitting function (1c) has to be used instead of (1b).

3. Results and discussion

In this work we present appearance energies (AEs) for cations formed by electron impact ionization of neutral CH_3D and CD_4 via the following reactions:

$$e + CH_3D \rightarrow CH_3D^+ + 2e \tag{2}$$

$$e + CH_3D \rightarrow CH_2D^+ + H^- + 2e \tag{3a}$$

$$e + CH_3D \rightarrow CH_2D^+ + H + 2e \tag{3b}$$

$$e + CH_3D \rightarrow CH_3^+ + D + 2e \tag{4}$$

$$e + CH_3D \rightarrow CHD^+ + H_2 + 2e \tag{5}$$

$$e + CD_4 \rightarrow CD_4^+ + 2e \tag{6}$$

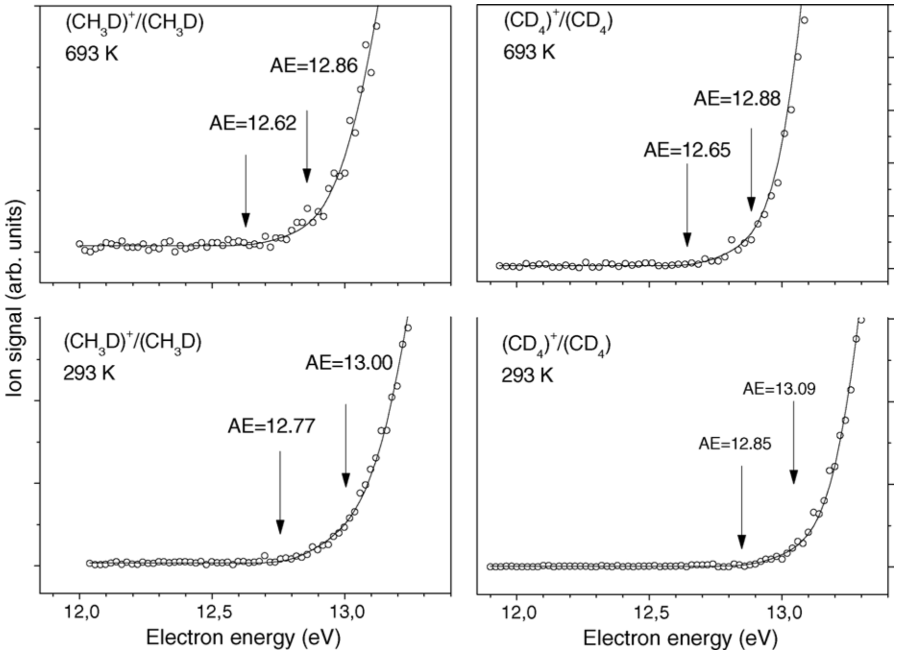

Fig. 2. Ion efficiency curves (open circles) of the parent ions $(CH_3D)^+/(CH_3D)$ (left) and $(CD_4)^+/(CD_4)$ (right) measured at the gas temperatures of 293 K (bottom) and 693 K (top), respectively. The fit curves are shown as solid lines. The AEs indicated by arrows are the thresholds for these individual data sets and differ from the AEs given in the text and in the tables which are derived by averaging several AE values from individual data sets.

$$e + CD_4 \rightarrow CD_3{}^+ + D + 2e \tag{7}$$

$$e + CD_4 \rightarrow CD_2{}^+ + D_2 + 2e \tag{8}$$

Examples for the measured ionization efficiency curves of all cations studied are shown in Figs. 2–4. All cations have been investigated at two different gas temperatures, 293 K and 693 K, respectively. The ion yields have been measured from about 1 eV below the threshold up to 1 eV above the onset. Employing the fitting method mentioned above the corresponding AEs have been derived. The results for cations of partially deuterated methane (CH_3D) measured at the gas temperature of 293 K are summarized in Table 1; those for fully deuterated methane (CD_4) are shown in Table 2. The present AE values in the tables and in the text were derived by averaging the results of several individually measured data sets and the uncertainties given were calculated as the difference between the largest and smallest value of the AE determined from these different measurements. Also included in Tables 1 and 2 are previously reported AE values (where available) using electron impact ionization [2,3] or photoionization [4,5]. Table 3 shows the isotope shift of the present AEs to the AEs of corresponding CH_4 cations which were reported previously by Stano et al. [11] using the same apparatus and same fitting procedure.

Table 1
AEs of cations formed via electron impact of neutral partially deuterated methane (CH_3D) at the gas temperature of 293 K

$e + CH_3D \rightarrow$	AE (in eV)	
	Present	EI[a]
$(CH_3D)^+$	12.75 ± 0.03 12.99 ± 0.03	13.12 ± 0.02
$(CH_2D)^+ + H^-$	13.66 ± 0.07	–
$(CH_2D)^+ + H$	14.42 ± 0.05	
$(CH_3)^+ + D$	14.54 ± 0.05	–
$(CHD)^+ + H_2$	15.22 ± 0.1	–

The present values for the parent cation is compared with the value obtained in Ref. [2] using electron impact (EI).

[a] Ref. [2].

3.1. CH_3D^+/CH_3D and $CD_4{}^+/CD_4$

The present ion efficiency curves of CH_3D^+/CH_3D and $CD_4{}^+/CD_4$ have a first weak onset at 12.75 ± 0.03 eV and 12.84 ± 0.02 eV, respectively, which is followed at about 0.23 eV above this first onset by a second threshold (see Fig. 1). We attribute these two thresholds in the ion efficiency curves to two different electronic states of the ion and have been observed already in the case of CH_4 molecule. The only previous AE value for the parent cation CH_3D^+/CH_3D was reported by Lossing et al. [2] using electron impact. They reported AE values for two different ion sources (where the differences of the sources consisted in the lens geometry and the extraction potentials), i.e., for CH_3D^+/CH_3D AEs of 13.12 ± 0.02 eV and 13.21 ± 0.02 eV, respectively. The lower value included in Table 1 is 0.37 eV higher than the present AE. They also determined the AE of $CD_4{}^+/CD_4$ (i.e., 13.26 ± 0.02 eV and 13.35 ± 0.02 eV), the lower value is more than 0.42 eV higher than the present value. Another value of the appearance energy for $CD_4{}^+$, also 0.37 eV higher than the present AE, was obtained by Honig [3] using electron impact ionization. This difference in the AE between the present work and the previous electron impact studies [2,3] could be due to the fact that the previous electron impact mea-

Table 2
AEs of cations formed via electron impact of neutral deuterated methane (CD_4) at the gas temperature of 293 K

$e + CD_4 \rightarrow$	AE (in eV)				
	Present	EI[a]	EI[b]	PI[c]	PI[d]
$(CD_4)^+$	12.84 ± 0.02 13.07 ± 0.03	13.26 ± 0.02	13.21 ± 0.02	12.65 ± 0.015	12.87 ± 0.02
$(CD_3)^+ + D$	– 14.54 ± 0.03	–	–	–	14.38 ± 0.03
$(CD_2)^+ + D_2$	15.41 ± 0.05	–	–	–	15.25 ± 0.04

The present values are compared with values obtained in electron impact works (EI) [2,3] and photoionization (PI) [4,5] studies, where available.

[a] Ref. [2].

[b] Ref. [3].

[c] Ref. [4].

[d] Ref. [5].

surements were performed with standard ion sources without an electron monochromator. In this case one can expect that the accuracy of these earlier measurements suffered from low energy resolution (> 0.5 eV).

For both parent cations, CH_3D^+/CH_3D and $CD_4{}^+/CD_4$, the two thresholds in the ion efficiency curve show a different isotope shift with respect to CH_4, i.e., the second onset exhibits a significantly smaller isotope shift than the first threshold (see Table 2 for the exact values). Moreover, for both thresholds of CH_3D^+/CH_3D a weaker isotope effect (increase) is observed as compared to CH_4 than for $CD_4{}^+/CD_4$. The present isotope effects for the first thresholds are similar to the shift observed in two previous electron impact works [2,3]. Moreover, agreement is also found with the isotope effect reported by Dibeler et al. [5] using photoionization. The most recent PI study by Berkowitz et al. [4] yielded an increase of 40 meV for the adiabatic ionization threshold when going from $CH_4{}^+$ to $CD_4{}^+$ much lower than observed in previous PI and photoelectron works [5–7]. The authors in [4] claimed that the stronger isotope effect in the adiabatic ionization energy reported in previous works is caused by smaller Franck Condon factors for CD_4 than for CH_4, i.e., it is more difficult to measure the adiabatic value and this leads to the higher reported adiabatic values of the IE in [5–7]. The present isotope shift is also much higher than the difference in zero point energy of CH_4 and CD_4 reported by [4]. The value of the AE for $CH_4{}^+$ by Stano et al. [11] lies close (40 meV higher) to the adiabatic value reported by Berkowitz et al. This is similar to previous observations for other simple molecules [19,1] like N_2O or H_2 where the AE determined in electron impact ionization measurements is close to the adiabatic value.

Table 3
Present shifts on the AEs of cations for CH_3D and CD_4 to the AEs of the corresponding cations for undeuterated methane (CH_4) [11] compared with previously determined shifts [7–10] using different experimental techniques like electron impact (EI) and photoionization (PI)

	Isotope shift (in meV)				
	Present	EI[a]	EI[b]	PI[c]	PI[d]
$(CH_3D)^+/CH_3D$	100 40	50			
$(CH_2D)^+/CH_3D$	80 80				
$(CH_3)^+/CH_3D$	200				
$(CHD)^+/CH_3D$	110				
$(CD_4)^+/CD_4$	190 120	170	170	50	160
$(CD_3)^+/CD_4$	200				130
$(CD_2)^+/CD_4$	310				90

[a] Ref. [2].

[b] Ref. [3].

[c] Ref. [4].

[d] Ref. [5].

For both parent cations a noteworthy temperature effect on the AE is observed, i.e., for CH_3D^+/CH_3D both onsets are about 180 meV lower at the higher gas temperature than at ambient temperature and for $CD_4{}^+/CD_4$ a decrease of about 230 meV is observed when going from 293 K to 693 K. The present temperature effects are higher than those reported for CH_4 (140 meV) [11]. In general the temperature effect can be explained by the increase of internal energy, i.e., higher vibrational and rotational states are populated at higher gas temperatures. Stano et al. [11] also calculated the increase of the average internal energy of the CH_4 molecule within the harmonic oscillator approximation and predicted a shift of 120 meV for CH_4 in good accordance with the measured value of 140 meV. For the present (partially) deuterated methanes the temperature effect is enhanced because the rotational-vibrational levels of CH_3D and CD_4 are energetically lower than in the case of CH_4 [20], i.e., higher rotational and vibrational levels are more populated at elevated gas temperature leading to larger shifts of the AEs. The harmonic oscillator approximation gives the internal energy increase between 293 K and 693 K of 130 meV in the case of CH_3D and 160 meV in the case of CD_4.

3.2. CH_2D^+/CH_3D and $CD_3{}^+/CD_4$

The ion efficiency curve of CH_2D^+/CH_3D reveals two onsets (see Fig. 2). The first onset is about 0.75 eV lower than the second one. This value corresponds to the electron affinity of H (EA = 0.75419 eV [16]), i.e., the first threshold can be ascribed to reaction (3a) involving H^- formation. Unfortunately, the ion yield CH_2D^+/CH_3D (mass 16 amu) is contaminated by a weak

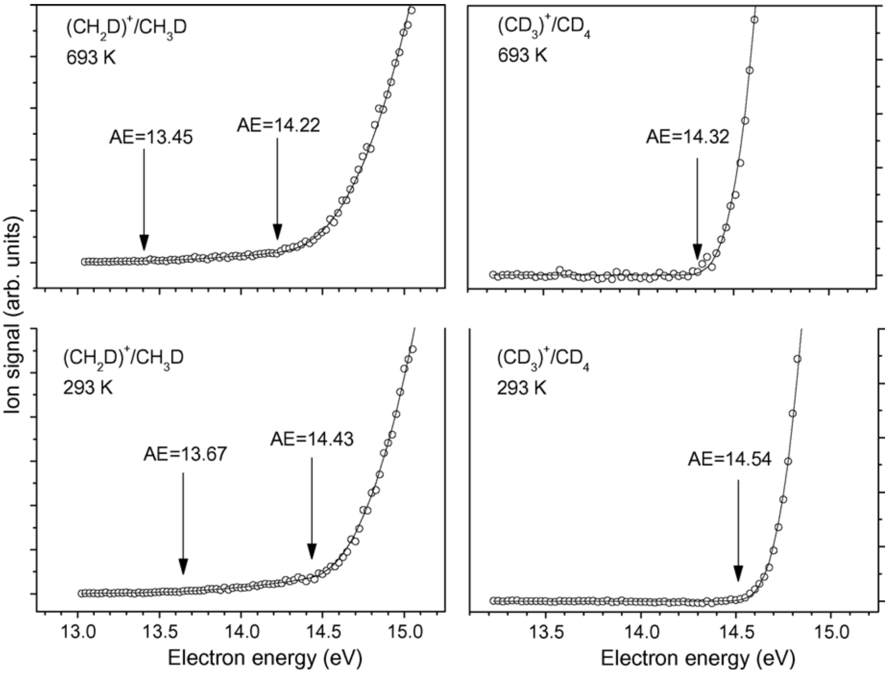

Fig. 3. Ion efficiency curves (open circles) of the fragments ions $(CH_2D)^+/(CH_3D)$ (left) and $(CD_3)^+/(CD_4)$ (right) measured at the gas temperatures of 293 K (bottom) and 693 K (top), respectively. The fit curves are shown as solid lines. The AEs indicated by arrows are the thresholds for these individual data sets and differ from the AEs given in the text and in the tables which are derived by averaging several AE values from individual data sets.

ion signal of CH_4^+/CH_4. CH_4 is present in small amounts as an impurity in the gas sample, and thus it is impossible to avoid this contamination. Nevertheless, it was possible to derive the first threshold of CH_2D^+/CH_3D using a special fitting procedure, in which the CH_4^+/CH_4 background has been subtracted from the CH_2D^+/CH_3D ion yield. For CH_2D^+/CH_3D an upward isotope shift with respect to the AE of CH_3^+/CH_4 [11] of about 80 meV is observed for both thresholds. Also the ion efficiency curve of CD_3^+/CD_4 (mass 18 amu) was affected by the presence of H_2O^+ due to ionization of water present as background in the chamber. In this case it was not possible to derive an onset using a special fit procedure which can be ascribed to $CD_3^+ + D^-$ formation,

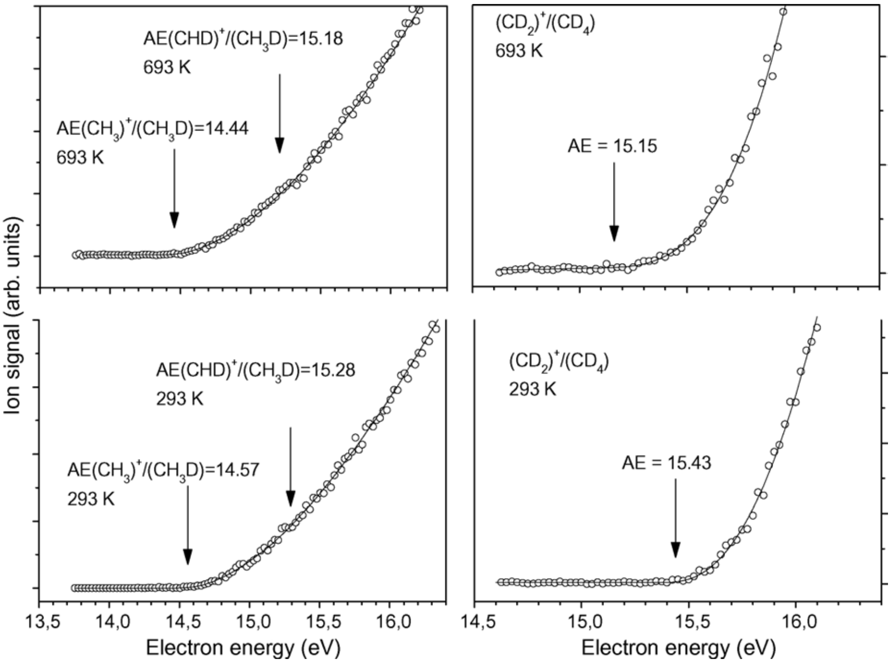

Fig. 4. Ion efficiency curves (open circles) of the fragments ions $(CHD)^+/(CH_3D)$, $(CH_3)^+/(CH_3D)$ (left) and $(CD_2)^+/(CD_4)$ (right) measured at the gas temperatures of 293 K (bottom) and 693 K (top), respectively. The fit curves are shown as solid lines. The AEs indicated by arrows are the thresholds for these individual data sets and differ from the AEs given in the text and in the tables which are derived by averaging several AE values from individual data sets.

Table 4
AEs for cations of CH_3D and CD_4 determined at different gas temperatures (290 K and 690 K)

	Present AEs at different gas temperatures (in eV)		
	AE(293 K)	AE(693 K)	AE(693 K) − AE(293 K)
$(CH_3D)^+/CH_3D$	12.75 ± 0.03 12.99 ± 0.03	12.58 ± 0.05 12.80 ± 0.07	0.17 ± 0.07 0.19 ± 0.08
$(CH_2D)^+/CH_3D$	13.66 ± 0.07 14.42 ± 0.05	13.49 ± 0.07 14.25 ± 0.05	0.17 ± 0.1 0.17 ± 0.06
$(CH_3)^+/CH_3D$	14.54 ± 0.05	14.42 ± 0.05	0.12 ± 0.05
$(CHD)^+/CH_3D$	15.22 ± 0.1	15.11 ± 0.1	0.11 ± 0.08
$(CD_4)^+/CD_4$	12.84 ± 0.02 13.07 ± 0.03	12.60 ± 0.04 12.84 ± 0.04	0.24 ± 0.06 0.23 ± 0.06
$(CD_3)^+/CD_4$	14.54 ± 0.03	14.31 ± 0.05	0.23 ± 0.04
$(CD_2)^+/CD_4$	15.41 ± 0.05	15.21 ± 0.05	0.2 ± 0.08

i.e., also after subtraction of the H_2O background ion signal no first threshold appears (see Fig. 3). Thus, it can be concluded that this reaction pathway is considerably weaker for CD_4 than for CH_3D and CH_4. For CD_3^+/CD_4 an isotope effect of 200 meV is observed which is 70 meV larger than the only previously value reported by Dibeler et al. using photoionization [5]. The decrease in the AE at the higher gas temperatures of 170 meV in the case of CH_2D^+/CH_3D and 230 meV for CD_3^+/CD_4 is nearly the same as for the corresponding parent cations (see Table 4.). A similar situation was also observed for undeuterated methane previously where the decrease of the AE for CH_3^+/CH_4 and the parent cation were reported (140 meV) [11].

3.3. CHD^+/CH_3D, CH_3^+/CH_3D and CD_2^+/CD_4

The ion efficiency curve of CHD^+/CH_3D (mass 15 amu) is shown in Fig. 4. Moreover, at this mass also the fragment cation CH_3^+/CH_3D may be present. Two thresholds have been found in the ion yield (Table 1), i.e., the first threshold (14.54 ± 0.05 eV) was tentatively ascribed to the latter cation because in this case only one C–D bond has to be broken. For CHD^+/CH_3D two C–H bonds have to be broken and thus a higher AE can be expected. The binding energy between a single C–H bond and a C–D bond differ only by 32.19 meV [21]. Also for CH_3^+/CH_3D (like for CD_3^+/CD_4) no corresponding D^- formation can be observed which would result in a second weak onset 0.75 eV below the main onset. However, the intensity for this fragment cation is generally already very low compared to the dehydrogenated methane cation and the ion pair formation may be below the detection limit of the apparatus used.

Noteworthy is the difference in the observed isotope effect. The ion yield CHD^+/CH_3D shows an upward shift of the appearance energy of 110 meV compared to the corresponding cation of undeuterated methane whereas for CH_3^+/CH_3D a shift of 200 meV is observed. The latter shift can be also derived for CD_3^+/CD_4 where also one C–D bond has to be broken for the formation of this fragment cation. For CD_2^+/CD_4 the largest isotope effect of all presently studied cations is observed, i.e., 310 meV which is 220 meV larger than the only previously value reported by Dibeler et al. [5]. The large value of the isotopic shift in the case of the CD_2^+/CD_4 results from the fact that two C–D bonds had to be broken in the course of this reaction. The value of the isotopic shift is then represented by the sum of two isotopic shifts for one bond break. The temperature effects for CHD^+/CH_3D, CH_3^+/CH_3D and CD_2^+/CD_4 is smaller than for the two other ions discussed above. The difference to the corresponding parent cations is about 50 meV, 60 meV and 40 meV, respectively. The lower values of the temperature shift may result from the fact that the cross-sections for these reaction channels are very low and thus also the precision of the threshold estimation is lower. Stano et al. [11] did not investigate the temperature effect on the AE of CH_2^+/CH_4.

4. Conclusions

We have determined the AEs of cations formed via electron impact of (partially) deuterated methane. For the determination of isotope effects the present values are compared with the AEs for CH_4 [11] determined previously with the same apparatus and the same fitting procedure. For all measured cations an isotope effect on the AE is observed. The isotope effect is larger for CD_4 than for CH_3D. From the present results several trends concerning the isotope effect on the AE can be deduced: (i) a smallest isotope effect is observed for the parent cations; whereas (ii) for fragment cations stronger isotope shifts are observed which become larger for smaller fragment cations. For fragment cations Dibeler et al. (photoionization) observed the reverse tendency, i.e., the AE isotope effect became weaker for smaller fragment cations [5]. The previous electron impact studies [2,3] reported a similar isotope shift for CD_4^+/CD_4 as in the present case. However, the previous AE values determined in electron impact experiments are much higher than the present AEs which can be explained by the different experimental conditions (energy resolution, etc.).

Using the temperature controlled neutral beam source the ionization efficiency curves were measured at two different gas temperatures, 293 K and 693 K. We observe a noteworthy temperature effect on the AE (decrease in AE with increasing temperature) for both molecules. For CD_4 the shift is larger than for CH_3D and in addition for both molecules the temperature effect is more pronounced than for CH_4.

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