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Electron impact ionization of acrylonitrile

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ABSTRACT

An electron impact (EI) ion source and a double focusing sector field mass spectrometer were used to investigate ionization processes of acrylonitrile C_3H_3N. The ionization and appearance energies for observed singly $C_xH_yN_z^+$ ($x = 1–3$; $y = 0, 1, 3$; $z = 0, 1$) and doubly $C_3H_3N^{2+}$ and C_3HN^{2+} charged ions were determined by using the non-linear least-square fitting procedure to the raising set of the data points. In the case of ions: $C_2HN^+/C_3H_3^+$, $C_2N^+/C_3H_2^+$, C_3H^+, C_3^+, CH_2N^+, $CHN^+/C_2H_3^+$, C_2H^+, C_2^+, H_2N^+, HN^+/CH_3^+, CH_2^+/N^+, CH^+, C^+, $C_3H_3N^{2+}$ and C_3HN^{2+} these energies were obtained for the first time.

1. Introduction

Acrylonitrile is not known to occur as a natural product and is produced commercially by propylene ammoxidation, in which propylene, ammonia, and air are reacted by catalyst in a fluidized bed. It can also be found in car exhaust and in cigarette smoke. Acrylonitrile is used extensively in the manufacture of synthetic fibres, plastics, polymers, surface coatings, nitrile elastomers, barrier resins, adhesives and in the synthesis of various antioxidants and pharmaceuticals. It is also a confirmed species in interstellar space [1–11].

The investigation of physical properties of the acrylonitrile molecule is being a subject of many investigator studies within the last few decades. For these investigations, several measurement techniques were applied: electron–ion coincidence, chemical ionization, resonant Auger electrons spectroscopy, charge exchange and electron spectroscopy [12–18]. Ionization of the acrylonitrile molecule was also a subject of many papers, however the main attention in these papers was devoted to determine the ionization energy (IE) of the parent molecule. For the wide spectrum of observed fragment ions created during the dissociative ionization in the ion source the majority of values of appearance energies (AE), i.e., minimum energy of the electrons in the ionizing beam necessary for the production of a given fragment ion are not reported [19–26].

In our laboratory the investigations of ionization processes and especially fragmentation reactions of ions initiated by electron impact (EI) of molecules plays a special role [27–36]. Just very scarce reported data for fragmentation reactions of acrylonitrile ions was for us direct encouragement for the investigations presented here. Therefore, in this work mass spectrometric investigations of ionization or appearance energies for all observed acrylonitrile ions produced by electron impact are presented. To our knowledge, this is the first time that threshold for appearance energies for all observed ions formed by electron impact of acrylonitrile have been measured on the apparatus using the same method.

2. Experimental

A high resolution double focusing sector field mass spectrometer of reversed Nier–Johnson type B-E geometry [27–33] with the Nier-type electron impact ion source was applied for the investigations presented here (Fig. 1). This spectrometer was described in detail previously [33–36]. Briefly, this apparatus is equipped with a channeltron-type based detection system and the vacuum system allows to work with a background pressure of 4×10^{-8} mbar. In the ionization chamber a magnetic field (magnet) is parallel to the electron beam axis. The electron energy is scanned in an automated stepwise mode with the energy increment of 0.1 eV

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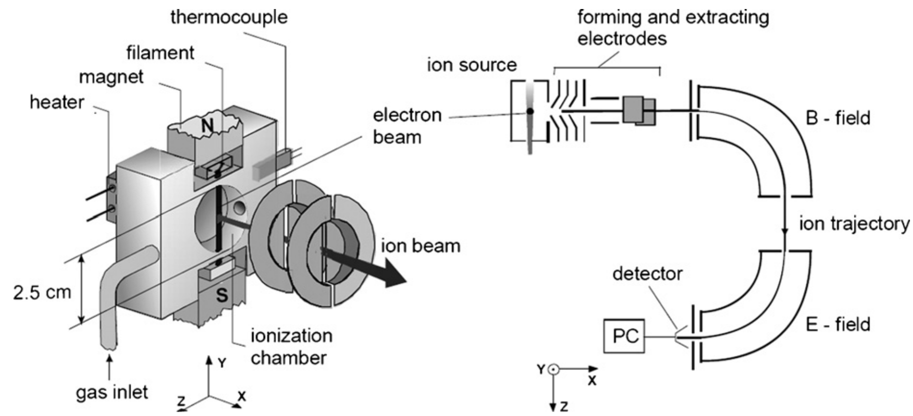


Fig. 1. Schematic view of the double focusing sector field mass spectrometer of reversed Nier–Johnson type B-E geometry with the Nier-type electron impact ion source.

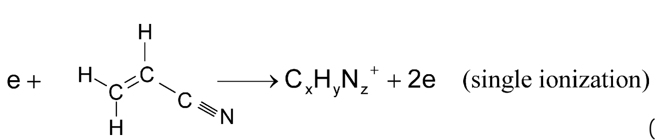
starting from 0 up to 100 eV. In the present experiment the electron beam current was set up to 0.3 mA for the mass spectrum measurements and 20–30 μA for the ionization energy scans. The ion source pressure is controlled by a Balzers Compact Full Range Gauge PKR 250 placed near the ionization chamber. The temperature of ionization chamber is controlled by the alumel–chromel thermocouple and is about 500 K at the typical working conditions.

In the present experiment liquid acrylonitrile (purity 99.5%, purchased from Sigma–Aldrich) is kept at a temperature of 310 K, and its vapor is introduced via a capillary leak gas inlet system into the collision chamber of the ion source. The neutral gas target at a pressure of 6×10^{-7} mbar is crossed by a well characterized magnetically collimated electron beam with FWHM energy spread of ~0.5 eV. For this pressure ion/molecule reactions in the ionization chamber are negligible and fast internal ion/molecule half reactions can take place, only [37–40].

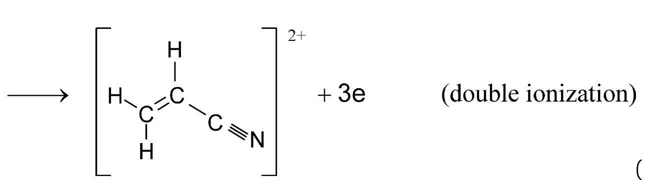
Ensuing cations are extracted by a weak electric field, pass through the system of the ion beam forming lenses (focusing and deflecting), than are accelerated to the mass spectrometer through a potential drop of $U_{acc} = 4$ kV and finally are detected by a channeltron-type electron multiplier.

3. Results

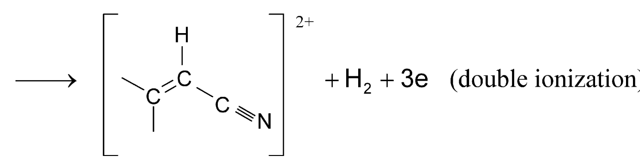
In all measurements described here, the temperature of ionization chamber has the established value of about 500 K. The typical electron impact mass spectrum of acrylonitrile taken at 100 eV electron energy is shown in Fig. 2. Ions originating from the residual gas in the background (4×10^{-8} mbar) were subtracted by mass spectra that were measured without acrylonitrile in the gas inlet system. For electron impact ionization of acrylonitrile C_3H_3N the following reactions can take place:



(1a)



(1b)



(1c)

where: $x = 1–3$; $y = 0, 1, 3$; $z = 0, 1$.

The mass spectrum of the acrylonitrile clearly reveals the presence of double charged ions at the mass to charge ratios $m/z = 26.5$ and 25.5 resulting from $C_3H_3N^{2+}$ (reaction (1b)) and C_3HN^{2+} (reaction (1c)), respectively (see Fig. 2c).

Peaks at the mass to charge ratios $m/z = 15$, 26, 27, 38 and 39 can correspond to pair of ions (HN^+/CH_3^+), ($CN^+/C_2H_2^+$), ($CHN^+/C_2H_3^+$), ($C_2N^+/C_3H_2^+$) and ($C_2HN^+/C_3H_3^+$), respectively, and separation of such ions is impossible at the present experiment.

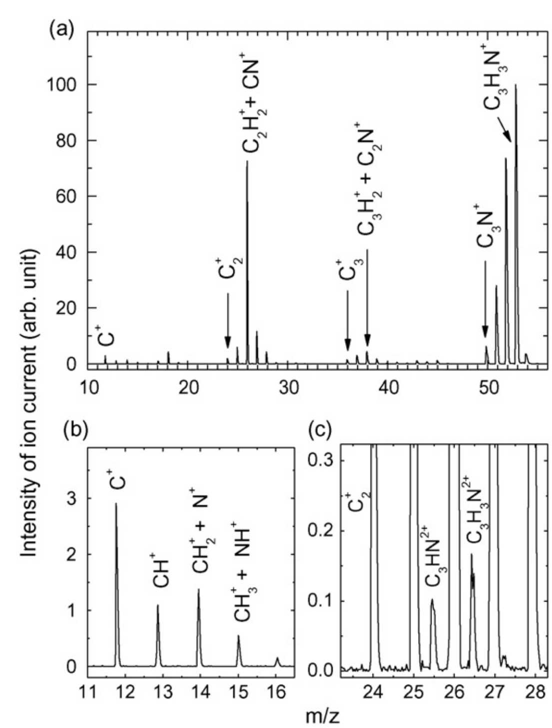
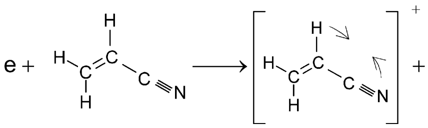


Fig. 2. Mass spectrum of acrylonitrile upon electron impact ionization: (a) full range spectrum, (b) detailed view for m/z ratio range from 11 to 16 and (c) doubly charged $C_3H_3N^{2+}$ and C_3HN^{2+} ions at $m/z = 26.5$ and 25.5, respectively. The electron ionization energy was $E_e = 100$ eV and the intensity of the electron beam $I_e = 0.3$ mA.

As it results from the chemical structure of the acrylonitrile molecule the ions HN^+, $CH_3{}^+$, H_2N^+, CHN^+ and CH_2N^+ can be formed via fast internal ion/molecule half reactions. For example, HN^+ can be formed from the $C_3H_3N^+$ parent ion via an internal ion/molecule reaction between H and N atoms (ions) and by the elimination of a C_3H_2 neutral (reaction (2)):



(2)

For all observed ions ionization or appearance energies were determined and results of our measurements are presented in Fig. 3. The electron energy scale was calibrated against the well-known threshold for the Ar^+ ion atom. For these calibrations the accuracy is better than ±0.5 eV. These energies have been determined by using the non-linear least-square fitting procedure to the raising set of data points. A good enough agreement between our measurement and literature values for the ionization energy of the $C_3H_3N^+$ encouraged us to undertake a similar study (appearance potentials) for all product of acrylonitrile. The presently determined values of ionization and appearance energies and results

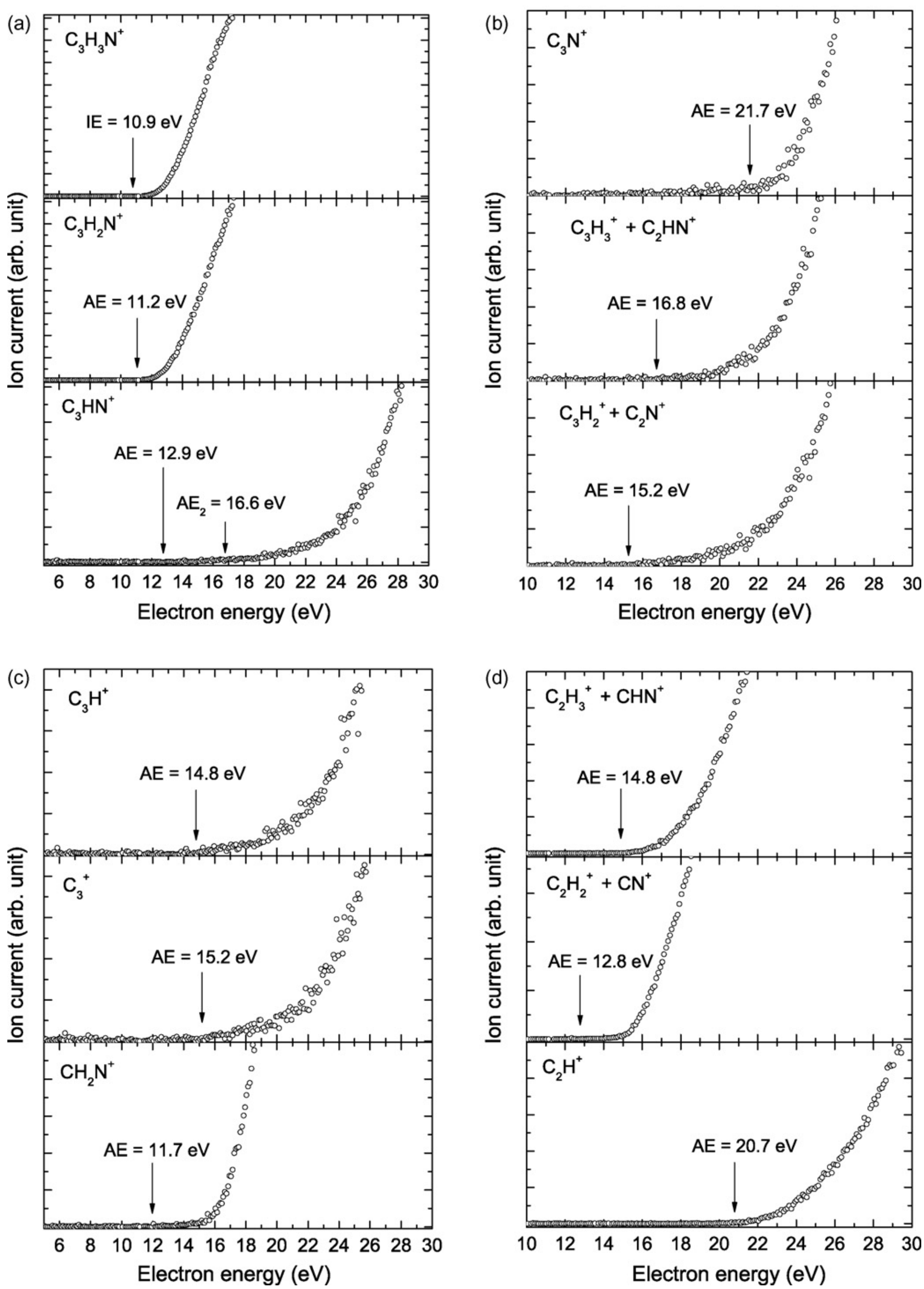


Fig. 3. Intensity of ion current as a function of the electron energy at the intensity of an electron current of $I_e = 20\ \mu A$: (a) $C_3H_3N^+$, $C_3H_2N^+$, C_3HN^+; (b) C_3N^+, $C_3H_3{}^+/C_2HN^+$, $C_3H_2{}^+/C_2N^+$; (c) C_3H^+, $C_3{}^+$, CH_2N^+; (d) $CHN^+/C_2H_3{}^+$, $CN^+/C_2H_2{}^+$, C_2H^+; (e) $C_2{}^+$, H_2N^+, $HN^+/CH_3{}^+$; (f) $CH_2{}^+/N^+$, CH^+, C^+; (g) $C_3H_3N^{2+}$, C_3HN^{2+}.

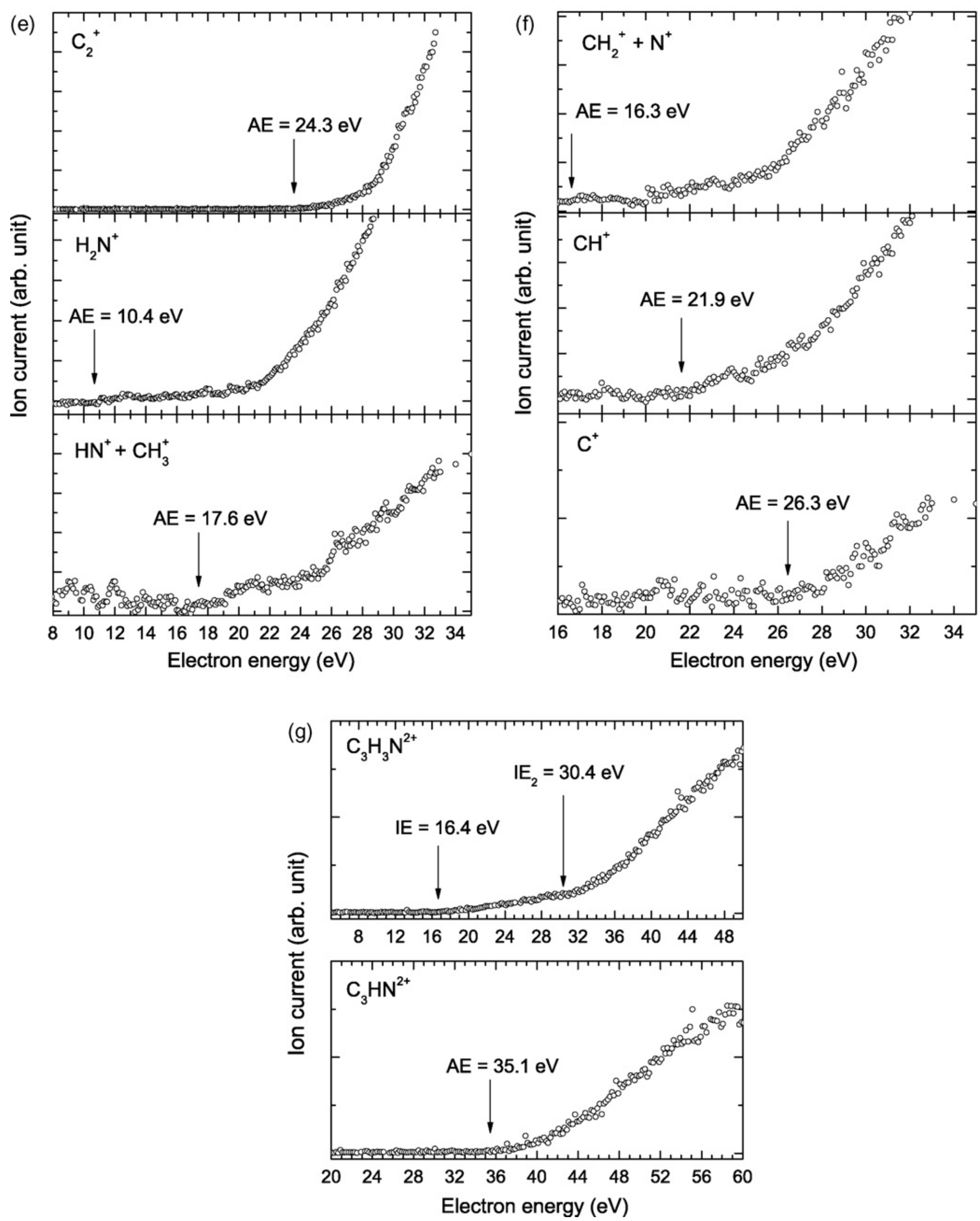


Fig. 3. (*Continued*).

obtained by the other authors who used different experimental methods (EI: electron impact; PI: photoionization; PE: photoelectron spectroscopy) are collected in Table 1. The literature values for the appearance energies were found just only for the most dominant ions, i.e., C_3HN^+ and C_3N^+ [26], and $C_3H_2N^+$ and pair $C_2H_2^+/CN^+$ [25]. All these values of the appearance energies were obtained by electron impact electron impact method. The analysis of the threshold regions for the $C_3H_2N^+$ and C_3N^+ (Fig. 3a and b) results in an appearance energies 11.9 ± 0.1 eV and 21.7 ± 0.1 eV, respectively. The present value of the appearance potential for the $C_3H_3N^+$ ion is much below the literature value. However, in Fig. 3a (the lowest panel) two thresholds are easily recognized in the ion yield curves. The second value of the appearance energy is $AE_2 = 16.6 \pm 0.2$ eV and is in good agreement with the value observed by Chelobov et al. [26]. Our value of $AE = 21.7 \pm 0.1$ eV for the C_3N^+ fragment ion is already in good agreement with the literature value.

For the ions: $C_3H_2N^+$ and pair $C_2H_2^+/CN^+$ our values of the appearance energies are below the values reported by Momigny et al. [25] (see Table 1). For all other observed fragment ions we have no literature data for comparison, however we can compare some fragment ions, i.e., C^+ CH^+ or C_2N^+ to vales of appearance energies of similar by groups ions formed from electron impact ionization of acetonitrile [41,42]. In both cases appearance energies for these C^+, CH^+ and C_2N^+ fragment ions are higher than 20 eV.

Ion yields shown in Fig. 3g represent the doubly ionized species: $C_3H_3N^{2+}$ and $C_3H_2N^{2+}$. For these ions our data analysis gives $IE = 16.4 \pm 0.2$ eV and $AE = 35.1 \pm 0.2$ eV, respectively. For the parent ion $C_3H_2N^{2+}$ we can also distinguish second threshold for the ionization energy, $IE_2 = 30 \pm 0.4$ eV. Up to our knowledge there is no atom or molecule where the removal of the second electron requires less energy than the removal of the first. Thus the lower IE = 16.4 eV we consider most likely as the foot of the singly charged species $C_2H_2^+$ or $C_2H_3^+$ which are close by and have similar

Table 1
Ionization and appearance energies

Ion	Other products	Ionization or appearance energies (eV)		
		This work	Method	Literature
$C_3H_3N^+$		10.9 ± 0.1	EI	
			PI	10.91 ± 0.01 [19]
			PE	10.91 [20]; 10.92 ± 0.05 [21]; 10.91[22]; 11.1 [23]; 10.91 [24]
$C_3H_2N^+$	H	11.2 ± 0.1	EI	13.82 ± 0.08 [25]
C_3HN^+	H_2	11.9 ± 0.1	EI	16.4 ± 0.1 [26]
C_3N^+	H_3	21.7 ± 0.1	EI	21.6 ± 0.1 [26]
$C_3H_3^+/C_2HN^+$	N/CH_2	16.8 ± 0.1	EI	
$C_3H_2^+/C_2N^+$	HN/CH_3	15.2 ± 0.1	EI	
C_3H^+	H_2N	14.8 ± 0.1	EI	
C_3^+	H_3N	15.2 ± 0.1	EI	
CH_2N^+	C_2H	11.7 ± 0.2	EI	
$CHN^+/C_2H_3^+$	C_2H_2/CN	14.8 ± 0.2	EI	
$CN^+/C_2H_2^+$	C_2H_3/CHN	12.8 ± 0.1	EI	13.13 ± 0.10 [25]
C_2H^+	CH_2N	20.7 ± 0.2	EI	
C_2^+	CH_3N	24.3 ± 0.2	EI	
H_2N^+	C_3H	10.4 ± 0.2	EI	
HN^+/CH_3^+	C_3H_2/C_2N	17.6 ± 0.2	EI	
CH_2^+/N^+	C_2HN/C_3H_3	16.3 ± 0.2	EI	
CH^+	C_2H_2N	21.9 ± 0.2	EI	
C^+	C_2H_3N	26.3 ± 0.2	EI	
$C_3H_3N^{2+}$		30.4 ± 0.4	EI	
C_3HN^{2+}	H_2	35.1 ± 0.2	EI	

EI: electron impact; PI: photoionization; PE: photoelectron spectroscopy.

threshold energies. Thus, the second value of the ionization energy $IE_2 = 30 \pm 0.4$ eV we consider as an energy necessary for doubly ionization of the parent molecule of acrylonitrile.

4. Conclusion

An electron impact ion source on a double focusing sector field mass spectrometer was used to investigate ionization and appearance energies for observed singly $C_xH_yN_z^+$ ($x = 1–3$; $y = 0$, 1, 3; $z = 0$, 1) and doubly $C_3H_3N^{2+}$ and C_3HN^{2+} charged ions from acrylonitrile. These energies have been determined by using the non-linear least-square fitting procedure. To our knowledge for the ions $C_2HN^+/C_3H_3^+$, $C_2N^+/C_3H_2^+$, C_3H^+, C_3^+, CH_2N^+, $CHN^+/C_2H_3^+$, C_2H^+, C_2^+, H_2N^+, HN^+/CH_3^+, CH_2^+/N^+, CH^+, C^+, $C_3H_3N^{2+}$ and C_3HN^{2+} these results are presented for the first time.

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