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Formation of Negative Ions upon Dissociative Electron Attachment to the Astrochemically Relevant Molecule Aminoacetonitrile

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Abstract

Aminoacetonitrile ($\text{NH}_2\text{CH}_2\text{CN}$; AAN) is a molecule relevant for interstellar chemistry and the chemical evolution of life. It is a very important molecule in the Strecker diagram explaining the formation of amino acids. In the present investigation, dissociative electron attachment to NH_2CN was studied in a crossed electron – molecular beams experiment in the electron energy range from about 0 eV to 17 eV. In this electron energy range, the following six anionic species were detected: $\text{C}_2\text{H}_3\text{N}_2^-$, $\text{C}_2\text{H}_2\text{N}_2^-$, $\text{C}_2\text{H}_2\text{N}^-$, C_2HN^- , CN^- , and NH_2^- . Possible reaction channels for all the measured negative ions are discussed and the experimental results are compared with calculated thermochemical thresholds of the observed anions. Similarly to other nitrile and aminonitrile compounds, the main anions detected were the negatively charged nitrile group, the dehydrogenated parent molecule and the amino group. No parent anion was observed. Low anion yields were observed indicating that AAN is less prone to electron capture. Therefore, AAN can be considered to exhibit a relatively long life time under typical conditions in outer space.

I. INTRODUCTION

The interest in studies on effects of the interaction between low energy electrons with biologically relevant molecules is steadily growing over the last years.¹⁻⁴ In this work, we report a study of electron attachment to aminoacetonitrile, $\text{NH}_2\text{CH}_2\text{CN}$, (denoted as AAN in the following), which is also referred to as cyanomethylamine or glycinenitrile in the literature. Recently, we studied the negative ion formation by the dissociative electron attachment to cyanamide.⁵ Cyanamide as well as AAN are representatives of a biologically relevant and very important group of aminonitriles. These compounds contain two significant organic groups, namely the amino (NH_2) and cyano (CN) groups. The former is a common

component of biomolecules like amino acids or proteins. In the case of AAN, additionally the methylene (CH_2) bridge is connecting the two groups mentioned. Therefore, $\text{NH}_2\text{CH}_2\text{CN}$ could also serve as a model molecule for more complex species with biological relevance. Hence, the results of our study are expected to contain information that may be transferable to these bigger biomolecules comprising the same functional groups.

AAN is an important molecule in astrophysics. It was observed in many astrophysical objects like gas clouds of the interstellar medium (ISM), e.g., Sagittarius B2,⁶ and atmospheres like those of the moon Titan⁷ where it is believed to be synthesized by heterogeneous chemistry. Among the various aminonitriles, AAN is of particular interest as it is one of the central molecules in the model route of amino acid synthesis.^{6,8} The first attempt to understand the pathways of AAN formation came from Strecker in 1854.⁹ The proposed series of reactions leading to the formation of AAN is called Strecker synthesis, which finally aims to explain the amino acid generation. Strecker proposed that the AAN could be formed in a series of the following reactions: (i) a reaction between aldehyde and ammonia in a liquid water environment in order to form the imine, (ii) a reaction between imine and hydrogen cyanide leading to the formation of AAN.

There were also attempts to estimate the age of the interstellar clouds from the consecutive addition of HCN (an abundant molecule in the ISM) to AAN. The age of an interstellar cloud might then be revealed by the time required for the growth of the longest observed chain in a molecular sequence.¹⁰

Danger et al.^{6,11} showed that formation of AAN from the thermal processing of ices containing methanimine, ammonia and hydrogen cyanide under conditions alike those in the ISM is possible. Moreover, Belloche et al.¹² showed that AAN may be formed by cyanogen hydrogenation or photochemically under astrophysical conditions from nitrile and ammonia mixtures. The subsequent hydrolysis of aminonitriles may lead then to amino acid formation.

Overall, many experiments on AAN formation were conducted at different, also astrophysical-like conditions, which confirmed that nitriles could promote the formation of amino acids.^{6,11-13} This is of special importance as earlier studies showed that AAN and other nitriles have much longer life times under outer space conditions than organic acids. The half-life for photodestruction of AAN is about 1330 years.¹⁴

By the reasons mentioned so far it is very interesting and important to study those mechanisms by which aminoacetonitrile may be dissociated through the interaction with a surface, ions, photons and like in the present studies, electrons. The motivation for investigations on the electron – aminoacetonitrile interaction is also directly related to processes in the interstellar medium (ISM) and to elementary steps in biological material, e.g. what happens with the molecule under irradiation.

Moreover, AAN as biologically relevant molecule has also some implication for living organisms. For example AAN was used as the inhibitor of glycine oxidation¹⁵⁻¹⁷ in the study of the involvement of the different electron transport paths in mitochondria. Therefore any investigation of the electron – AAN molecule interaction may help with the understanding of the processes proceeding in the cells of any living organisms. In these studies again the connection between the AAN and glycine is mentioned. The AAN and its derivatives are also of interest as structural elements for drug design.¹⁸

Although AAN seems to be an essential compound in many aspects, data rarely exist on the electron impact leading to the formation of positive ions.¹⁹ Using a residual gas analyser quadrupole mass spectrometer, the vapour of AAN, desorbing from an icy surface at a temperature of 200 K, was ionized by an electron beam at the electron energy of 70 eV. In the m/z (mass/charge) range from 20 to 60, three major groups of ions were observed in the obtained mass spectrum. These m/z regions were 25 to 31, 38 to 41 and 52 to 57. The most abundant ions at $m/z = 28, 29, 55, 56$ (corresponding to the parent ion: $\text{NH}_2\text{CH}_2\text{CN}^+$) and 27

were detected. A similar electron impact ionization mass spectrum (with the mentioned three relevant m/z regions) is also obtainable from the NIST web page.²⁰ However, significant differences exist in the ion current intensities of the NIST data and the above mentioned study,¹⁹ although the same ionization method was applied in both of them. In the NIST data, there are only two major peaks corresponding to the AAN parent ion (m/z 56) and the fragment at m/z = 55 resulting from the loss of H atom from AAN; the latter ion has higher intensity.

In the low electron energy range (<15 eV), electron attachment is an important process, which may lead to destruction of a molecule via dissociative electron attachment (DEA). To the best of our knowledge, there is no data available regarding the formation of negative ions by electron attachment to AAN. This additionally encouraged us to perform studies of low energy electron attachment and to determine ion efficiency curves as well as resonance energies for the most abundant fragment anions formed in free electron capture by AAN.

II. EXPERIMENTAL

The experiments were carried out using an established experimental setup in the Institute of Ion Physics and Applied Physics at the University of Innsbruck. The electron attachment spectrometer used in the present studies comprises a molecular beam source, a Nier type ion source and a double focussing mass spectrometer with combined magnetic and electric sector fields with a pulse counting system for detecting the ionic products. This apparatus has been described in detail previously.²¹ Briefly, AAN, being liquid at room temperature, was first introduced to the inlet system of the mass spectrometer. As the vapour pressure of AAN at room temperature is high enough, evaporated AAN molecules were admitted through a copper capillary of 1 mm I.D. to the ion source. At this sample

temperature the pressure in the main vacuum chamber of the mass spectrometer was about 10^{-6} mbar ensuring collision-free conditions. In the ion source, the AAN molecular beam was crossed with the electron beam. The electron current was set to 10 μ A and regulated to this value above the electron energy of about ~ 2 eV. The anions generated by the electron attachment process were extracted by electrostatic fields to the mass filter, where they were analysed and detected by a channeltron type secondary electron multiplier. The $\text{NH}_2\text{CH}_2\text{CN}$ sample of 98% purity was purchased from Sigma Aldrich, Vienna, Austria.

In order to determine the energy spread of the electron beam and to calibrate the electron energy scale, the well-known cross sections for the formation of SF_6^- , F_2^- , and F^- by electron attachment to SF_6 were used.²² The resonances of all three anions were used for calibration of the electron energy scale whereas the ~ 0 eV resonance of SF_6^- was used to determine the electron energy spread (the apparent FWHM – full width at half maximum – represents the energy resolution of the electron beam). In the present experiments the FWHM was 0.8 eV. The accuracy of peak maxima reported here is about ± 0.2 eV. Moreover, we note that the onsets of resonances are shifted downwards due the beam energy spread. Therefore we estimated the experimental threshold by a linear fit of the left tail of the resonance and extrapolation to zero ion yield. We estimate the accuracy of the thresholds to ± 0.4 eV.

III. QUANTUM CHEMICAL CALCULATIONS

To complement and support the analysis and interpretation of the experimental results, we used the well-established high-level extrapolation scheme W1BD²⁵ for the calculation of (adiabatic) electron affinities (EA) and thermochemical reaction thresholds (TRT). W1BD²⁵ is considered to yield very high accuracy and achieves a mean absolute deviation from experiment of 0.48 kcal/mol for a variety of properties (like atomization energies, electron

and proton affinities, etc.) assembled in the G2/97^{26,27} test set. This extrapolation scheme was used also in the mentioned previous study on cyanamide.⁵ The reaction thresholds have been obtained as the difference between all ground state energies of the reaction products (anionic and neutral fragments) and reactants (i.e., here, the parent molecule). The computed electron affinities are summarized in Table 1. In the following section, the derived reaction thresholds ΔE are mentioned for the specified reaction channels. All quantum chemical calculations have been carried out using the Gaussian 09 software.²⁸

Table 1. Adiabatic electron affinities (EA) for the $\text{NH}_2\text{CH}_2\text{CN}$ molecule and relevant neutral fragments as obtained with the W1BD extrapolation scheme.

Electron affinities for molecules/atoms	W1BD [eV]	NIST [eV] [16]
$\text{NH}_2\text{CH}_2\text{CN}$	-0.85	
NHCH_2CN	1.55	
NH_2CHCN	0.95	
NH_2CCN	0.59	
NCH_2CN	0.34	
NHCHCN	0.38	
$\text{NH}_2\text{CH}_2\text{C}$	0.93	
NH_2CH_2	-0.63	
NH_2CN	-0.80	
CH_2CN	1.55	1.53
CHCN	2.55	2
CH_3CN	-1.14	0.01
N_2H_4	-1.22	
C_2H_2	-1.55	

C ₂ H ₄	-1.69	
NH ₃	-1.35	
NH ₂	0.75	0.77
NH	0.34	0.37
N	-0.18	
CN	3.90	3.86
CH ₄	-1.28	
CH ₃	0.029	0.08
CH ₂	0.64	0.65
CH	1.21	1.24
C	1.25	1.26
H	0.29	0.75

IV. RESULTS AND DISCUSSION

Electron attachment to AAN is a purely dissociative process yielding production of six anionic fragments at m/z of 55 (C₂H₃N₂⁻), 54 (C₂H₂N₂⁻), 40 (C₂H₂N⁻), 39 (C₂HN⁻), 26 (CN⁻), 16 (NH₂⁻). The possibility of a stable negatively charged AAN parent ion was previously predicted in calculations (MP2/TZVP), in which the EA value of 0.07 eV for the AAN molecule was obtained.²⁹ In our experimental studies the parent anion NH₂CH₂CN⁻ was not observed within the detection limit of the apparatus and also the W1BD calculations result in a negative adiabatic EA value for AAN of -0.85 eV. Due to this discrepancy between the results of our calculations and the ones from the earlier study,²⁹ we repeated the calculations at the MP2/TZVP level of theory. We obtained the same geometries of the neutral AAN molecules as well as the anion. However, for the adiabatic EA we obtained -1.90 eV in line with the negative adiabatic EA obtained using W1BD.

In Figure 1 the anion yield curves for all observed negatively charged fragments in the electron energy range of about 0 up to 17 eV are presented. The intensities are given in arbitrary but reproducible units, i.e. the ion signals for all anions are comparable. Table 2 summarizes the present results concerning the resonance peak positions. In the following paragraphs we will discuss in detail possible production mechanisms for all fragment anions which have been detected.

Table 2. Peak positions of resonances observed in the ion yield of fragment anions obtained in dissociative electron attachment to $\text{NH}_2\text{CH}_2\text{CN}$.

Ion	Observed resonance maxima in eV (uncertainty ± 0.2 eV)
CN^-	1.9 and 5.6
NH_2^-	5.6 and ~ 9.4
$\text{C}_2\text{H}_3\text{N}_2$	3.2 and 5.2
$\text{C}_2\text{H}_2\text{N}^-$	~ 2 , 2.9, 5.4, 10.8, ~ 15
$\text{C}_2\text{H}_2\text{N}_2^-$	2.5 and 5.6
C_2HN^-	1.3, 2.4, 5.6, 8.3, 10.8

Figure 1. Fragment anions observed in DEA to $\text{NH}_2\text{CH}_2\text{CN}$.

CN⁻

The observation of the CN⁻ anion in DEA to AAN is of special importance. This negative ion is the smallest molecular anion detected in space.³⁰ Hence, it is important to know the possible pathways of CN⁻ formation. Related to this issue its generation from AAN may have some implications to the understanding of CN⁻ occurrence in the ISM, especially if we take into account that, according to our data, the CN⁻ anion is the most efficiently formed anion in DEA to AAN. This result is in line with our previous studies of DEA to acetonitrile and cyanamide^{5,31} with the CN⁻ as the most intensively generated anion. We also note that this is further in agreement with other studies of electron attachment to different nitrile molecules (C₂H₃CN, C₆H₅CN and CF₃CN),^{32,33} where the CN⁻ anion was the major or one of the major ions observed. However, despite of the high electron affinity of CN (3.90 eV – see Table I), the ion counting rates of CN⁻ in the DEA to AAN are rather low compared to the halogen anions formed by DEA to halogenated molecules. It is also worth to add here, that in the CN⁻ ion yield no resonances at very low energies (~ 0 eV) are present as in the case of halogenated molecules. Using ab initio calculations, this situation has been explained for previously investigated nitrile molecules by considering their molecular orbital structures and energies.³³ The highest occupied molecular orbital of radical anions of the nitriles is π^* antibonding with virtually all the additional charge localized at the nitrile group, resulting in a reduction of the C≡N bond dissociation energy. The CN⁻ ion generation is hence associated with the energy transfer from the C≡N bond to R-CN bond, where dissociation into CN⁻ and the radical R in their electronic ground state is symmetry forbidden. For that reason it can only occur through pre-dissociation of the parent anion, and thus the cross section for formation of CN⁻ is relatively low considering the high electron affinity value of CN. The calculations of vibrational frequencies^{34,35} for AAN also correspond to the above assumption of a

predissociation process in the temporary negative ion. These indicate that the C-C bond stretching mode is most probably involved in the excitation of intense oscillations in the AAN molecule case, promoting also this bond disruption. The latter will lead to the formation of CN and NH₂CH₂ fragments or in the present case to one fragment in the anionic form depending on the particular EA. The measured low CN⁻ yields are in line with the assumption of a required predissociation process.

In the present study the CN⁻ ion is formed at two major resonance electron energies peaking at 1.9 eV and 5.6 eV. 14 possible reactions exist leading to the formation of the CN⁻ anion. These DEA channels together with the calculated reaction energy thresholds (ΔE) are:

All reaction channels are endothermic in the range between 0.99 eV for reaction (1a) up to 20.74 eV for (1o). The appearance energies (AE) derived from the experimental CN^- ion yield curve are 1.0 eV for resonance at 1.9 eV and 4.0 eV (resonance at 5.6 eV), respectively. Based on our calculations of the reaction energy thresholds, the first resonance (at 1.9 eV) can be assigned to the single AAN bond cleavage reaction channel (1a), with the computed ΔE of 0.99 eV. In the case of the higher energy resonance (with AE of 4.0 eV) in the CN^- ion yield, reaction channels (1b) and (1c) may be considered. In reaction (1c) two hydrogen atoms are transferred from the amino group to form methane, which means that a complex molecular rearrangement is required to be involved. Due to the latter and since CN^- formation is characterized by the highest ion yield, we investigated this reaction channel computationally in more details. We calculated several local minima and transition states along a reaction path on the potential energy surface connecting the ground state of AAN with the final fragmentation products methane, atomic nitrogen and CN^- , see Figure 2. Geometries, harmonic frequencies and zero-point energy corrections have been calculated at the B3LYP/cc-pVTZ+d level of theory,^{36,37} whereas energies have been refined at the CCSD(T)/aug-cc-pVTZ level of theory.^{37,38} Along the considered reaction path, first, a C-N bond is broken upon electron attachment resulting in a neutral H_2NCH_2 molecule (Figure 2(c)) and the CN^- anion with an energy of about 0.96 eV above the energy of the neutral AAN (Figure 2(b)) in close agreement with the W1BD result of 0.99 eV. In a next step, a hydrogen atom is transferred from the amino group in the H_2NCH_2 molecule to the CH_2 group such that HNCH_3 (Figure 2(e)) is formed with an energy of 1.21 eV above the reference energy of the neutral AAN. This proceeds via a transition state (TS1) (Figure 2(d)) which lies 2.81 eV above the reference. In order to form methane and atomic nitrogen, another transition state

(TS2) has to be passed (Figure 2(f)) with an energy of 4.81 eV above the reference. The latter actually appears too high having in mind the appearance energy of 4.0 eV. We note that the accuracy of the used method may be assumed to be rather high (in the order of 2-3 kcal/mol; about 0.08-0.13 eV) for equilibrium geometries but this cannot be assumed safely also for the transition states though. Therefore, we rather tend to ascribe the second resonance to reaction (1b) with a barrier of 2.81 eV. We also observed a broad tail for the second resonance up to the maximum energy considered (about 16 eV). Hence, other reactions (1c-1n) may be involved in CN^- generation at energies above 5.6 eV; however, no defined structure can be recognized in the ion signal.

Figure 2. (a) Reaction path connecting the neutral parent molecule AAN with the fragments methane, atomic nitrogen and CN^- . Geometries of the local minima and transition states obtained at the B3LYP/cc-pVTZ+d level of theory are shown for (b) neutral AAN, (c) H_2NCH_2 , (d) transition state TS1, (e) HNCH_3 , (f) transition state TS2.

NH_2^-

The NH_2^- ion is the second most efficiently formed anion in the low energy electron interaction with AAN; however, its intensity at peak maximum is ~12 times lower than for CN^- . Beside CN^- , it is the second distinctive anion formed by DEA to aminonitriles.⁵ As the EA of NH_2 is only 0.77 eV which is significantly lower than the EA of the CN molecule of 3.90 eV (see Table 1), this rather low difference in these two anion intensities additionally support the above explanation of the CN^- anion formation route. The negative ion of the amino radical (NH_2) may be formed via the following reaction channels:

The amide anion generation occurs in a strong resonance with the appearance energy of 4.7 eV and maximum at 5.6 eV. In the ion yield curve, also a second resonance starting at 7.5 eV and peaking at about 9.4 with lower intensity is apparent. Within the observed resonances for the amide anion it can be assumed that its formation is related to the reactions (2a - 2c). The calculations yield reaction energy thresholds at 2.63 eV, 7.17 eV, and 7.40 eV for these DEA channels (2a - 2c), respectively. Taking this into account, only the first reaction

(2a) associated with single bond dissociation may be responsible for the formation of NH_2^- at the main resonance. The formation of the amide anion at the resonance of 9.4 eV may be associated with the DEA channels (2b - 2d).

$\text{C}_2\text{H}_3\text{N}_2^-$ and $\text{C}_2\text{H}_2\text{N}_2^-$

Similar to earlier studies of electron capture by other nitriles³¹⁻³³ also in the case of AAN, anions formed by the abstraction of one hydrogen atom, $\text{C}_2\text{H}_3\text{N}^-$, or two hydrogen atoms or a hydrogen molecule, $\text{C}_2\text{H}_2\text{N}^-$ are detected. Positive ions with the same stoichiometry were also observed in the mass spectrum with the $\text{C}_2\text{H}_3\text{N}_2^+$ as ones of highest intensity.^{11,19,20} The $\text{C}_2\text{H}_3\text{N}_2^-$ anion yield is almost the same as for NH_2^- one (its yield is of about 14 times lower with respect to CN^-).

The $\text{C}_2\text{H}_3\text{N}_2^-$ anion may be formed via two channels where the hydrogen atom is abstracted from the methylene or amino group:

The experimental data clearly indicate the existence of two possible resonance energies at which the $\text{C}_2\text{H}_3\text{N}_2^-$ anion is produced. There are two peaks observed at 3.2 eV and 5.2 eV, for which the anion yield at the resonance at lower energy is almost three times larger than at the 5.2 eV maximum. Considering the calculated ground state energies of AAN and fragments involved in reactions (3a and 3b) the energy thresholds for the channels have been derived as 2.64 eV and 2.86 eV, respectively. The (M-H)⁻ (M denoting the parent molecule) formation efficiency curve provides values of 2.3 eV and 4.3 eV of the experimental $\text{C}_2\text{H}_3\text{N}_2^-$ appearance energies for both resonances detected. Comparing the obtained AEs of anions with the calculated ΔE s, we notice that the experimental AE for the low energy resonance is

slightly lower than the ΔE for reaction (3a). If we take into consideration the accuracy of AE estimation we may affirm that the (3a) reaction is responsible for this resonance. The appearance energy for the second resonance lies above both thermochemical thresholds for the reactions (3a) and (3b). Hence, the 5.2 eV resonance can be attributed to the formation of excited NH_2CHCN^- anion via both channels. In the study of positive ionization of AAN the ion at $m/z = 55$ (M-H) was attributed to the same fragment structure NH_2CHCN^+ .¹¹

The $\text{C}_2\text{H}_2\text{N}_2^-$ ion yield is even lower than that of $\text{C}_2\text{H}_3\text{N}_2^-$. The ion yield ratio for these ions is equal of 0.17. This significant change in the anion beam intensity may be explained by the number of the C-H and N-H bonds which have to be broken in order to form the corresponding anions. In case of $\text{C}_2\text{H}_2\text{N}_2^-$ two H atoms must be cleaved from the AAN molecule and therefore the following reaction channels may be considered to explain its formation:

As in the AAN molecule two groups containing H atoms are present, six (4a-4f) reaction channels can be responsible for $\text{C}_2\text{H}_2\text{N}_2^-$ ion formation in three different structures: NHCHCN^- , NCH_2CN^- and NH_2CCN^- . The total energy balance is in favour of H atom abstraction from both, amino and methylene groups of AAN. In that case, depending on the neutral fragments formed H_2 (4a) or 2H (4d) the thermodynamic thresholds are equal of 0.79

eV and 5.27 eV, respectively. Very similar, but a little larger ΔE s are calculated for the channels (4b, 4e) for which both H atoms are separated from the amino group of AAN. These reaction thresholds are obtained as 0.85 eV and 5.34 eV for the respective channels with generation of neutrals H_2 (4b) or $2H$ (4e). The highest energy is needed to open the channels of the $C_2H_2N_2^-$ formation where the two C-H bonds are broken in the methylene group of the AAN molecule. Depending on neutral product (H_2 or $2H$) reactions (4c) and (4f) are endothermic by 1.89 eV and 6.30 eV, respectively.

The experimental $C_2H_2N_2^-$ ion yield shows that the formation of this anion is characterized by a major low energy resonance yielding the AE of 1.6 eV and the maximum at 2.5 eV. Also the second, minor and higher energy resonance with appearance energy of 4.6 eV, peaking at 5.2 eV appears in this anion yield curve. These data show that for the 2.5 eV resonance reactions (4a, 4b and as well 4c) are energetically accessible and hence we can ascribe the first $C_2H_2N_2^-$ resonance to these reaction channels. However from the energetic point of view, DEA channels with the lower reaction threshold (4a and 4b) are most probably responsible for formation of $C_2H_2N_2^-$ at 2.5 eV resonance. Due to the low difference in the thermochemical energy thresholds (0.79 eV, and 0.85 eV) of reaction 4a and 4b it is impossible to clearly state which one from these anion formation routes is most likely responsible for $C_2H_2N_2^-$ generation at this energy. The higher energy resonance (5.2 eV) is most probably associated with the channel (4c) in which the neutral hydrogen molecule is formed by the breaking two single C-H bond in the methylene part of the AAN. Additionally, one of the reactions 4a or 4b, most probably with the higher ΔE may be also responsible for $(M-H_2)^-$ generation. In that case the products of such a DEA reaction will carry on the excess energy ($AE - \Delta E$) by molecular excitation or kinetic energy. Based on the above assumptions the $C_2H_2N_2^-$ formation is most probably associated with the formation of molecular hydrogen. Mass spectrometric studies of Ni^+ ions reacting with AAN

in the gas phase have shown that the loss of H₂ molecule from AAN is also a very effective process in the case of positive ion formation.³⁹

C₂H₂N⁻ and C₂HN⁻

The C₂H₂N⁻ and C₂HN⁻ anions were also detected in the present studies of DEA to AAN. Concerning these anions, the DEA process includes the loss of one nitrogen atom from the neutral parent molecule and simultaneous bond breaking associated with two or three hydrogen atoms.

The reactions leading to C₂H₂N⁻ anion formation read as follows:

The intensity of the anion yield for C₂H₂N⁻ is ~33 times lower than that of CN⁻, placing C₂H₂N⁻ in fourth position of generated anions from AAN. The measured C₂H₂N⁻ signal shows that this anion is formed within a broad energy region between about 0.5 to 17 eV. We recognize one major resonance at 5.4 eV. Additionally, closer inspection in this anion yield indicates further low intensity resonances: two at low and one at high energy regions above 10 eV. In the 0.5 to 4 eV regime there are observable resonances at about 2.0 eV and 2.9 eV, whereas at higher electron energy we can distinguish also a resonance with maximum of ~10.8 eV. Moreover, a very low anion signal is observed at energies from 13 eV to 17 eV. The resonance at low energy appeared at 0.1 eV which is definitely below all calculated reaction thresholds. Therefore, this low intensity anion signal most probably corresponds to the DEA process to some impurity leading to the formation of anion yield at the same

nominal mass like $\text{C}_2\text{H}_2\text{N}^-$. The main resonance has the appearance energy of 4.3 eV. Within the calculated thermochemical thresholds, the 5.4 eV resonance may be attributed to reaction (5a) with ΔE of 1.84 eV. The reaction (5a) is complementary to the channel (2a) describing the NH_2^- anion formation. The shapes of both resonances (2a and 5a) are different. In particular, the signal of $\text{C}_2\text{H}_2\text{N}^-$ decreases more gradually than NH_2^- . This may be an indication that in the former case other resonances can be involved. However, considering the AEs and ΔE s for both (2a and 5a) DEA channels it may be concluded that they are characterised by the high excess energy of $\sim 2\text{eV}$. This energy excess may also be used for the further decomposition of the anion formed. Such decomposition promotes rather bigger than smaller fragments changing also the shape of its anion yield, like in our case. The existence of the higher energy resonance (10.8 eV) would correspond to the occurrence of $\text{C}_2\text{H}_2\text{N}^-$ anion formation via reactions (5b and 5c) with the thermochemical thresholds of 4.8 and 5.88 eV, respectively. The measured signal at energies above 13 eV may be also related to the channel (5d) with the calculated threshold of 9.30 eV, where all neutral fragments generated are in atomic form.

The C_2HN^- anion has the lowest intensity of all anions formed by DEA to AAN. The yield is about a factor 1000 times lower than the CN^- yield. The possible DEA channels at which C_2HN^- is formed are:

The measured C_2HN^- anion signal shows that this anion is formed within a broad energy region between about 0 to 17 eV with five resonances at 1.3 eV, 2.4 eV, 5.6 eV, 8.3 eV and 10.8 eV, and with a long tail up to about 17 eV. The plurality of resonance features leading to the C_2HN^- anion generation ratifies that this ion formation proceeds also via electron attachment to different states of the electronically excited molecule. In C_2HN^- anion formation, where additional energy in comparison to $\text{C}_2\text{H}_2\text{N}^-$ formation is needed for the H atom separation, we, surprisingly, obtained an ion signal at $m/z = 39$ in the low electron energy region from about 0 to 4 eV. The lowest threshold energy for C_2HN^- formation via reaction (6a) is 1.25 eV and hence considerably above the ion yield observed experimentally. Hence, we ascribe the ion yield observed in the region between 0 to 4 eV rather to an impurity. The third recognized resonance (at 5.6 eV) has the appearance energy of 4.2 eV, therefore it may be associated with the reaction (6a) where the neutral ammonia molecule is formed in addition to the C_2HN^- anion. The highest signal intensity was measured for the resonance at 8.3 eV with the experimental appearance energy of 6.0 eV. By comparison with the calculations we ascribe the 8.3 eV peak to the (6b and 6c) DEA channels. Due to the electron beam energy resolution, clear evidence which of these reactions is responsible or dominant is impossible. In relation to the number of the bonds needed to be broken in the AAN molecule the reaction (6b) is less probable than (6c). In DEA channel (6b), 3 bonds have to be broken and additionally one hydrogen molecule has to be generated, whereas in the reaction (6c) only 2 bonds are disrupted. In case of the resonance with the maximum at about 10.8 eV and the appearance energy of 9.0 eV the reaction (6d) with the thermodynamical threshold of 8.86 eV may be involved. The low anion signal above 10.8 eV peak may indicate that also the remaining channels may play some role in this anion generation.

V CONCLUSIONS

Dissociative electron attachment to aminoacetonitrile (AAN), an important astrophysical compound, was studied in the gas phase using electron attachment spectroscopy. The present study has shown that six anionic species are formed via DEA to AAN in the electron energy range of about 0 eV to 17 eV. For all possible anion fragments the DEA routes leading to the formation of respective negative ions are provided and thermochemical thresholds are calculated. Similarly to the earlier studies of other aminonitriles, also in the case of $\text{NH}_2\text{CH}_2\text{CN}$ the CN^- , NH_2^- and $(\text{M}-\text{H})^-$ are the most abundant fragment anions measured. The respective anion signals intensities are rather low, indicating a resistivity of AAN to electron capture induced dissociation and probably a long half-life time in space-like environments. AAN is suspected to be of significant relevance in the formation process of amino acids in the ISM. Therefore, we think that our investigation, in which AAN is irradiated with low energy electrons, is important also for a deeper understanding of such processes in the ISM.

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