

# Dissociative electron attachment to nitroethane: $C_2H_5NO_2$

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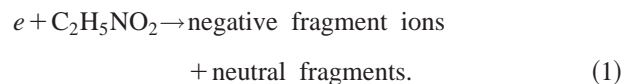
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Dissociative electron attachment (DEA) to nitroethane ( $C_2H_5NO_2$ ) in the gas phase is studied using a crossed electron–molecule beams technique. The ion yields for particular fragment ions were measured in the electron energy range from 0 to 9.5 eV with an electron energy resolution of about 120 meV. In contrast to previous studies additional negative ions, i.e.,  $HCN^-$  and  $NO^-$ , were observed. Measures for the absolute partial cross sections were obtained for the ions using a calibration technique involving a comparison with the known cross section of the 0.8 eV peak in DEA to  $CCl_4$ . The dominant negative ion product is  $NO_2^-$  with a cross section of approximately  $11 \times 10^{-22} \text{ m}^2$  at 0.75 eV. The values of the cross section estimates for the other ions are about  $\sigma(C_2H_3NO_2^-) = 4 \times 10^{-24} \text{ m}^2$  at  $\sim 0 \text{ eV}$ ,  $\sigma(O^-) = 5 \times 10^{-24} \text{ m}^2$  at 5.7 eV,  $\sigma(OH^-) = 2 \times 10^{-24} \text{ m}^2$  at 5.7 eV,  $\sigma(CN^-) = 5 \times 10^{-25} \text{ m}^2$  at 1.7 eV,  $\sigma(CNO^-) = 3 \times 10^{-25} \text{ m}^2$  at  $\sim 4.5 \text{ eV}$ ,  $\sigma(HCN^-) = 2 \times 10^{-25} \text{ m}^2$  at  $\sim 4.5 \text{ eV}$  and  $\sigma(NO^-) = 3 \times 10^{-25} \text{ m}^2$  at  $\sim 8 \text{ eV}$ . © 2003 American Institute of Physics. [DOI: 10.1063/1.1607314]

## INTRODUCTION

Nitro-organic compounds are molecules with a significant potential for industrial use. Electron interactions with these nitro-organic compounds, in particular electron attachment, may play an important role in plasma technological processes. Therefore, we have recently carried out a study<sup>1</sup> concerning dissociative electron attachment (DEA) to the simplest nitro-organic molecule, nitromethane. Although nitroethane is also a prototypical nitro-organic compound, it has been so far of considerably less interest to research than nitromethane. We are aware of only two previous DEA studies concerning nitroethane.<sup>2,3</sup> Jäger and Henglein<sup>2</sup> performed in 1967 a first experimental study concerning DEA to nitroethane in an electron energy range from about 0 to 10 eV using a sector field mass spectrometer with a pulsed Fox electron impact ion source with an estimated energy spread of less than 200 meV. They observed six fragment negative ions ( $NO_2^-$ ,  $C_2H_3NO_2^-$ ,  $O^-$ ,  $OH^-$ ,  $CN^-$ ,  $CNO^-$ ) and gave rough estimates of the corresponding cross sections. Tsuda *et al.*<sup>3</sup> employing a mass spectrometer without an electron monochromator to improve the energy spread from a rhenium filament measured the negative ion yields for the negative ions  $NO_2^-$ ,  $CH_2NO_2^-$ ,  $O^-$ ,  $CN^-$  and  $CNO^-$  in the electron energy range from about 3 to 30 eV. They were not able to measure the negative ion yield below 3 eV. There exist several discrepancies between the results of these two studies concerning the observed negative ions and also concerning the electron energy positions of some of the observed resonances.

In order to clarify these discrepancies, we have investigated in the present work DEA to nitroethane with an increased electron energy resolution and increased ion detection efficiency in the electron energy range from about 0 to 9.5 eV. We were able to observe eight negative fragment ions ( $NO_2^-$ ,  $C_2H_3NO_2^-$ ,  $O^-$ ,  $OH^-$ ,  $CN^-$ ,  $CNO^-$ ,  $HCN^-$  and  $NO^-$ ) formed by DEA to  $C_2H_5NO_2$  via



The present negative ion yields are in very good agreement with the data of Jäger and Henglein<sup>2</sup> (for the 6 negative ions measured in that experiment) concerning the overall shape of the ion yield curves and the positions of the resonances. In the present study we have, however, observed the formation of two additional negative fragment ions, i.e.,  $HCN^-$  and  $NO^-$ . Nevertheless we were not able to observe the  $CH_2NO_2^-$  ion detected by Tsuda *et al.*<sup>3</sup> Using a calibration technique, described in the Experiment section, we have derived the absolute partial cross sections for DEA to nitroethane.

## EXPERIMENT

The present studies have been performed with a crossed electron/molecular beams apparatus (Fig. 1) as described previously in detail.<sup>4</sup> The electron beam is formed in a trochoidal electron monochromator (TEM).<sup>5</sup> When measuring the fragments anions except for  $NO_2^-$ , we used a gas mixture of nitroethane and  $CCl_4$  of a mixing ratio of 23:1. In the case of  $NO_2^-$ , due to its large cross section and in order to check any interference with the calibration gas we used a ratio of 10:1 and also pure nitroethane. The pressure in our main chamber (which closely resembles the pressure in the collision chamber) was usually kept in the range of about  $10^{-6} \text{ mbar}$  in order to minimize secondary reactions (it should be mentioned that we did not see any sign of a

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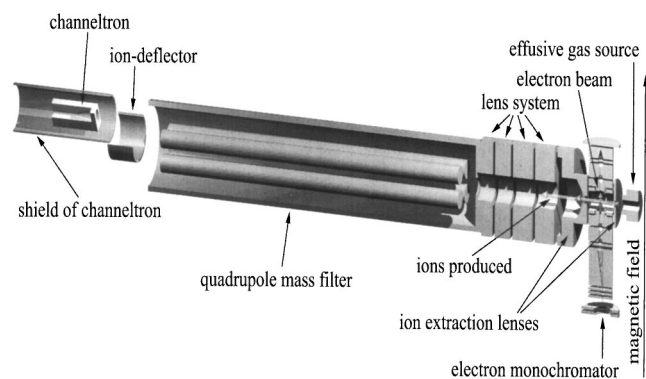


FIG. 1. Experimental setup.

$\text{C}_2\text{H}_2\text{NO}_2^-$  ion signal which according to Ref. 2 would be the product of an ion molecule reaction). The energy resolution (which can reach values under optimized conditions of about 30 meV) was set here to 120 meV at an electron current of 45 nA, thus allowing us to detect ions even with a small cross section. In order to extract the anions produced in the collision region towards the entrance of the quadrupole mass spectrometer (QMS), we applied a moderate, symmetric extraction potential of  $\pm 1$  V (corresponding to an extraction field of about 80 V/m) in all cases, in order to avoid the deterioration of the energy resolution and energy calibration by the fields. The mass selected negative ions were detected by a channeltron and the pulses processed using a pulse counting technique and computer. The intensity of a mass selected negative ion was recorded as a function of the electron acceleration voltage. The electron energy was calibrated using the DEA reaction,



The cross section for reaction (2) increases dramatically as the electron energy decreases,<sup>6</sup> yielding a prominent “zero eV peak.” The position of this peak was used for the calibration of the electron energy scale and the apparent width of this peak as a measure of the electron energy resolution of the electron beam (see Ref. 7). We calibrated the electron energy axis also by fixing the zero point at the electron acceleration voltage, where the electron current as a function of the acceleration voltage measured on a Faraday cup positioned after the collision chamber, was half its maximum value. These two methods were in good agreement concerning the electron energy scale calibration and also electron energy resolution (when using a retarding field energy analyzer in front of this Faraday detector).

Reaction (2) exhibits a second resonance at 0.8 eV with a cross section value of  $5 \times 10^{-20} \text{ m}^2$  (Ref. 8) and this value has been used to obtain rough estimates for the DEA cross sections for nitroethane. The procedure was as follows (and has been described in Ref. 1). The  $\text{Cl}^-$  ion yield from reaction (2) and the negative ion yields for reaction (1) have been measured at known partial pressures of  $\text{CCl}_4$  and  $\text{C}_2\text{H}_5\text{NO}_2$  in a given mixture. All measurements were performed at the same electron current. From a comparison of the intensities of the product ions of reaction (1) with the intensity of  $\text{Cl}^-$  ion at the maximum of the 0.8 eV resonance, an approximate

TABLE I. Absolute partial cross sections obtained in the present study and by Jäger and Henglein (Ref. 2) and for a comparison the cross sections of nitromethane obtained recently (Ref. 1).

Fragment ion	Nitroethane (present) $\sigma(\text{m}^2)$	Nitroethane (Ref. 2) $\sigma(\text{m}^2)$	Nitromethane (Ref. 1) $\sigma(\text{m}^2)$
$\text{NO}_2^-$	$7 \times 10^{-22}$	$3 \times 10^{-21}$	$\sim 10^{-21}$
$\text{C}_2\text{H}_3\text{NO}_2^-$	$4 \times 10^{-24}$	$1 \times 10^{-24}$	-
$\text{CH}_3\text{NO}_2^-$	-	-	$\sim 10^{-23}$
$\text{O}^-$	$5 \times 10^{-24}$	$3 \times 10^{-23}$	$\sim 10^{-23}$
$\text{OH}^-$	$2 \times 10^{-24}$	$\sim 0.8 \times 10^{-23}$	$\sim 10^{-24}$
$\text{CN}^-$	$5 \times 10^{-25}$	$4 \times 10^{-24}$	$\sim 10^{-24}$
$\text{CNO}^-$	$3 \times 10^{-25}$	$\sim 2 \times 10^{-24}$	$\sim 10^{-25}$
$\text{HCN}^-$	$2 \times 10^{-25}$	-	-
$\text{NO}^-$	$3 \times 10^{-25}$	-	-

measure of the partial cross sections for DEA to  $\text{C}_2\text{H}_5\text{NO}_2$  can be derived. For this calibration procedure we have neglected discrimination effects for ions in the reaction chamber due to their different kinetic energy (for more details on this see a recent study from our lab on the discrimination of fragment anions from ozone<sup>9</sup>) and assume constant transmission efficiency through the QMS and identical detection efficiencies for  $\text{Cl}^-$  and for the product ions of reaction (1). It is clear that all of these effects add up to considerable errors in the cross sections determined, and thus the present cross section values can only be considered to give an order of magnitude. It is interesting to note in this conjunction that cross sections (for all the small fragment anions) determined in the present study (see Table I) are in general lower than the ones reported by Jäger and Henglein<sup>2</sup> (using a pulsed extraction with a much higher extraction field of 1000 V/m), the only exception being the cross section for the heaviest anion  $\text{C}_2\text{H}_3\text{NO}_2^-$  where the present cross section lies a factor of about 4 above that from Ref. 2. This indicates that the studies have apparently opposite detection efficiencies for small (possibly energetic) and large (possibly thermal) ions.

## RESULTS AND DISCUSSION

Electron attachment to nitroethane in the gas phase proceeds only dissociatively and results in a variety of negative ions:  $\text{C}_2\text{H}_3\text{NO}_2^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}^-$ ,  $\text{CNO}^-$ ,  $\text{CN}^-$ ,  $\text{HCN}^-$ ,  $\text{OH}^-$  and  $\text{O}^-$ . These ions are observed in reasonable amounts in the electron energy region below 10 eV (see Figs. 2–4 and Table I). Note that the ion yields of negative ions formed by simple bond cleavages ( $\text{NO}_2^-$  and  $\text{O}^-$ ) have similar shapes and magnitudes in nitromethane (see Ref. 1) and nitroethane. In Table I the values of the cross sections for the DEA to nitroethane as obtained in the present experiment are presented. Also shown are the estimates taken from Jäger and Henglein.<sup>2</sup> It can be seen that most of the present cross section values are lower, only the cross section for  $\text{C}_2\text{H}_3\text{NO}_2^-$  is larger than the values given by Jäger and Henglein. Nevertheless, taking into account errors inherent to both experimental methods agreement only within an order of magnitude is not too surprising.

In the following we will describe results concerning the particular DEA channels.

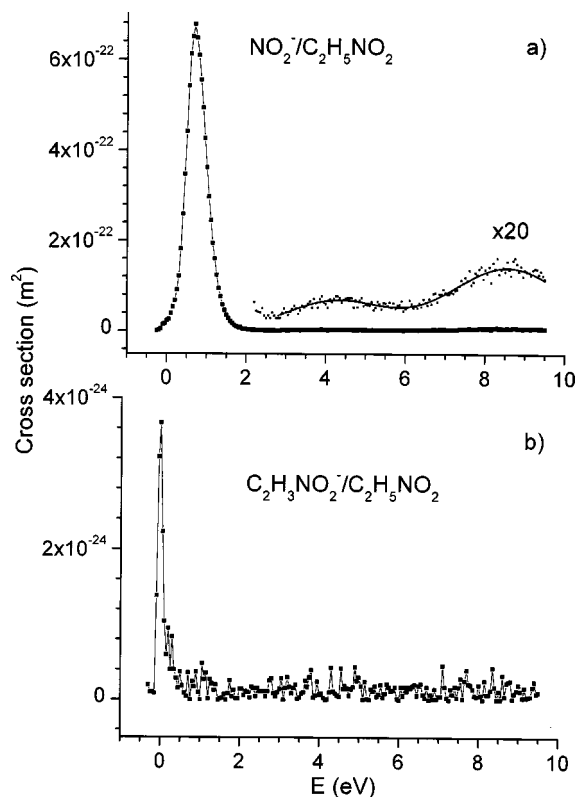


FIG. 2. Ion yields for the (a)  $NO_2^-$  and (b)  $C_2H_3NO_2^-$  channels of DEA to nitroethane. The full line is a fit to the data to guide the eye.

### A. $NO_2^-$

The most abundant negative ion observed in DEA to nitroethane is  $NO_2^-$ , formed via reaction

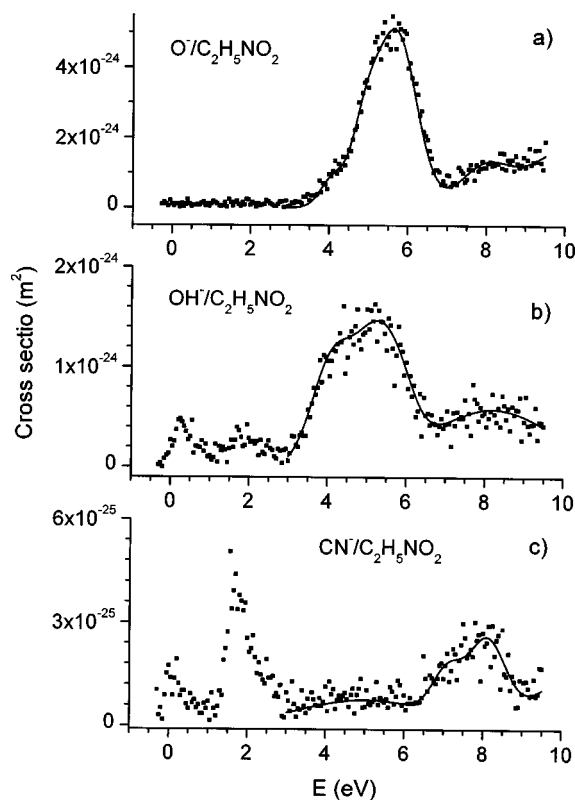


FIG. 3. Ion yields for the (a)  $O^-$ , (b)  $OH^-$ , and (c)  $CN^-$  channels of DEA to nitroethane. The full line is a fit to the data to guide the eye.

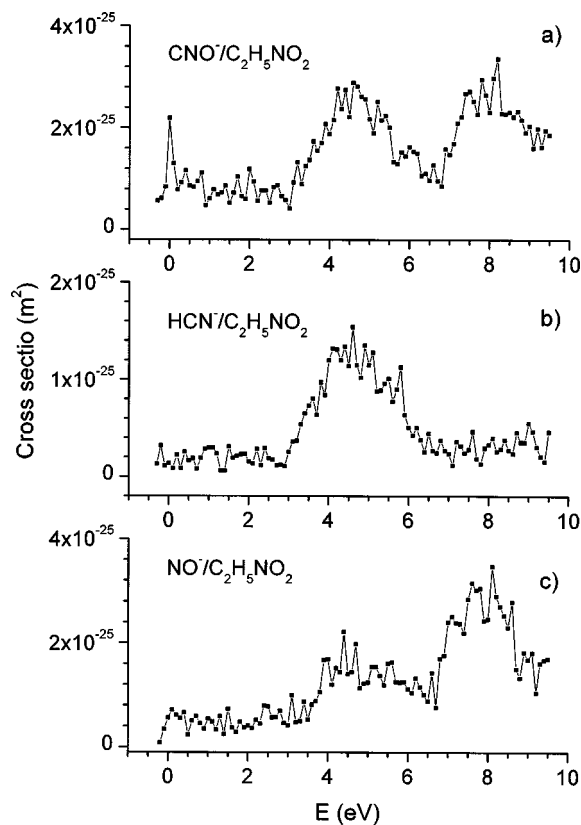
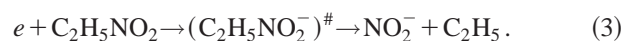


FIG. 4. Ion yields for the (a)  $CNO^-$ , (b)  $HCN^-$ , and (c)  $NO^-$  channels of DEA to nitroethane.

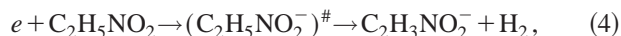


The measured ion yield is presented in Fig. 2. The DEA channel (3) is dominant almost in the whole electron energy range, with the exception of a narrow interval around 5.6 eV, where the  $O^-$  ion is the most abundant product ion. In the  $NO_2^-$  ion yield three resonances can be distinguished, i.e., at around 0.75, 4.5, and 8.5 eV. The 0.75 eV resonance is reminiscent of the 0.6 eV resonance in nitromethane.<sup>1,10</sup> Moreover, this resonance was observed also in nitroethane by Jäger and Henglein<sup>2</sup> (though peaking at approximately 1 eV), Tsuda *et al.*<sup>3</sup> were not able to measure any ion yields below 3 eV. The 0.6 eV resonance in nitromethane was attributed<sup>1</sup> to electron capture into the lowest virtual MO with a localized NO antibonding character [negative ion state  $(CH_3NO_2^-)^{\#}$  with  $\pi_{NO}^*$  character] and the formation of  $NO_2^-$  was then associated with an internal energy transfer from the N–O to the C–N coordinate. The mechanism of the formation of  $NO_2^-$  from nitroethane is most probably similar to that in nitromethane, i.e., the accommodation of the electron in an orbital with  $\pi_{NO}^*$  character and intramolecular energy transfer in the transient negative ion  $(C_2H_5NO_2^-)^{\#}$  to the C–N coordinate of nitroethane. The 4.5 eV resonance is most probably associated with an electronically excited state of the nitroethane anion, which has also an N–O antibonding character, as the resonance is observed also in the case of the  $O^-$  and  $OH^-$  ion. The formation of the  $NO_2^-$  at the 4.5 eV may be associated with formation of an excited  $C_2H_5^{\#}$  radical (as proposed by Tsuda *et al.*<sup>3</sup> based on arguments given by

Schulz<sup>12</sup>). The 8.6 eV resonance may correspond to the DEA involving the formation of multiple neutral fragments, or as proposed by Tsuda *et al.*<sup>3</sup> due to ion pair formation. It is interesting to note that the corresponding energy positions for the 4.5 and 8.5 eV resonance are given by Tsuda *et al.*<sup>3</sup> as 5.4 and 9.7 eV. Jäger and Henglein<sup>2</sup> did not present any ion yield for this DEA above 2.5 eV. They estimated the cross section for the 1 eV electron energy resonance to be about  $3 \times 10^{-21} \text{ m}^2$ , which is about four times larger than the present value.

### B. $\text{C}_2\text{H}_3\text{NO}_2^-$

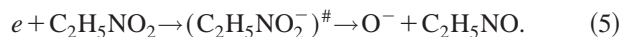
As shown in Fig. 2 we have observed the formation of  $\text{C}_2\text{H}_3\text{NO}_2^-$  ion via the following reaction:



at zero electron energy. This DEA proceeds apparently through the capture of *s*-wave electrons to nitroethane and the formation of the TNI  $(\text{C}_2\text{H}_5\text{NO}_2^-)^\#$  and a subsequent decomposition in  $\text{C}_2\text{H}_3\text{NO}_2^-$ . In nitromethane, analogous negative ions ( $\text{CHNO}_2^-$ , or  $\text{CH}_2\text{NO}_2^-$ ) were not observed. From the nonexistence of an analogous anion in nitromethane,  $\text{CHNO}_2^-$ ,  $\text{CH}_2\text{NO}_2^-$ , it may be concluded that the electron affinities (EA) for the  $\text{CHNO}_2$ , or  $\text{CH}_2\text{NO}_2$ , radicals are negative, i.e., the relevant negative ions are thermodynamically unstable. Conversely, an observation of the  $\text{C}_2\text{H}_3\text{NO}_2^-$  indicates, that the  $\text{EA}(\text{C}_2\text{H}_3\text{NO}_2^-)$  has a positive value. From the measured ion yield we are not able to deduce directly the structure of  $\text{C}_2\text{H}_3\text{NO}_2^-$ . The sole formation of the ion at 0 eV indicates that the channel (4) is exothermic. In the course of the reaction two C–H bonds have to be broken. If we assume that  $\text{BE}(\text{C–H}) \sim 4.5 \text{ eV}$ <sup>11</sup> then about 9 eV are necessary for this cleavage. Thus, at least 9 eV of energy must be regained by (i) the rearrangement of the bonds in the products (the formation of a double bond in the  $\text{C}_2\text{H}_3\text{NO}_2^-$  and the formation of a  $\text{H}_2$  molecule), and (ii) via the electron affinity of the  $\text{C}_2\text{H}_3\text{NO}_2$  radical. The value of the electron affinity of  $\text{C}_2\text{H}_3\text{NO}_2$  is not precisely known, but according to Ref. 13,  $\text{EA}(\text{C}_2\text{H}_3\text{NO}_2) > 1.65 \text{ eV}$ , and it should not exceed the value  $\text{EA}(\text{NO}_2) = 2.3 \text{ eV}$ .<sup>13</sup> According to Ref. 13,  $\text{BE}(\text{H}_2) = 4.54 \text{ eV}$ , and thus by the formation of a double bond in  $\text{C}_2\text{H}_3\text{NO}_2$  (e.g.,  $\text{H}_2\text{C}=\text{CHNO}_2$ , nitroethene) an energy of about 2.11–2.81 eV has to be gained. The typical C–C single bond energy in hydrocarbons is around 3.8 eV and the C=C double bond at around 7.5 eV, thus approximately 3.7 eV can be gained by changing the single to a double bond in accordance with the above calculations. The value of the cross section for the formation of this ion is about  $4 \times 10^{-24} \text{ m}^2$  and is about four times larger than the value given by Jäger and Henglein.<sup>2</sup> It is interesting to note that Tsuda *et al.*<sup>3</sup> do not report the production of this anion (they do not measure below 3 eV) and Jäger and Henglein<sup>2</sup> place the peak position approximately 0.2 eV above zero energy. This discrepancy to the present results is not too surprising given their larger energy spread and it is also in line with the energy difference observed for the  $\text{NO}_2^-$  product ion.

### C. $\text{O}^-$

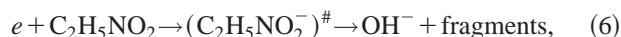
The formation of the  $\text{O}^-$  ion results via a simple bond cleavage:



The ion yield for  $\text{O}^-$  formation is presented in Fig. 3. The cross section curve of this anion is dominated by one major peak located between 3 and 7 eV and a slightly increasing cross section above this energy. The appearance energy of the  $\text{O}^-$  ions (in vanishing current approximation) is  $3.2 \pm 0.2 \text{ eV}$  and within the error bars is identical with the appearance energy of  $\text{O}^-$  from nitromethane ( $3.3 \pm 0.2 \text{ eV}$ ), which indicates that the values of the N–O bond energies in both molecules are very close. The value of the appearance energy is in good agreement with a value estimated by Tsuda *et al.* of 3.0 eV. It can be seen that the broad structure between 3 and 7 eV has an asymmetric shape. The shape of the structure resembles strongly a similar structure in  $\text{O}^-/\text{CH}_3\text{NO}_2^-$  and also the energies of the resonances are very similar. We assume that similarly as in nitromethane, these three resonances are associated with three different excited states of the TNI. Above 7 eV an increase of the  $\text{O}^-$  ion yield is observed with a small structure at about 8 eV. The  $\text{O}^-$  ion yield presented by Jäger and Henglein<sup>2</sup> exhibits resonances and structures which agree very good with the present data, however, there exists a discrepancy concerning the value of the cross section for DEA at the 5.7 eV resonance. The value estimated by Jäger and Henglein<sup>2</sup> of  $3 \times 10^{-23} \text{ m}^2$  is about six times larger than the present value of about  $5 \times 10^{-24} \text{ m}^2$ . Tsuda *et al.*<sup>3</sup> identified in their ion yield curve two resonances with maxima located at 6.7 eV and 10.2 eV, the position of the resonances disagree with the present observation and also with data from Ref. 2.

### D. $\text{OH}^-$

The formation of  $\text{OH}^-$  via DEA to nitroethane (Fig. 3) is the following:



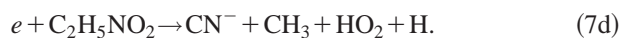
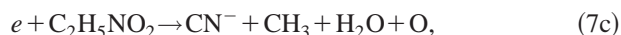
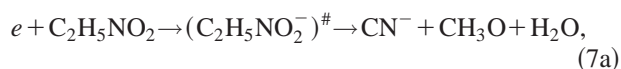
is associated with the dissociation of the O and H atom from the nitromethane and subsequent formation of an  $\text{OH}^-$  ion. The  $\text{OH}^-$  ion is observed at several resonances. In contrast to the study by Jäger *et al.*<sup>2</sup> who did not report any  $\text{OH}^-$  signal below 3.5 eV, here the formation of  $\text{OH}^-$  occurs already at low energies (with a first resonance at about 0.2 eV and the second at about 2 eV). From the point of view of energetics, the most favorable reaction involves the formation of the two neutral fragments acetonitrile ( $\text{CH}_3\text{CN}$ ) and OH. According to thermodynamic data in Ref. 13 [ $\Delta_f H_g^\circ(\text{C}_2\text{H}_5\text{NO}_2) = 103 \pm 0.4 \text{ kJ/mol}$ ,  $\Delta_f H_g^\circ(\text{OH}) = 38.99 \text{ kJ/mol}$ ,  $\Delta_f H_g^\circ(\text{CH}_3\text{CN}) = 74.04 \text{ kJ/mol}$  and  $\text{EA}(\text{OH}) = 1.828 \text{ eV}$ ] reaction (6) is exothermic. Both the 0.2 eV and the 2 eV resonances are located above this threshold and therefore it is reasonable to assume that acetonitrile and OH are indeed the neutral products. It is interesting to note that therefore acetonitrile can be formed from nitroethane by low energy electrons. The formation of the  $\text{OH}^-$  at higher electron energies (resonances at about 5 and 8 eV) is most



probably associated with strong fragmentation of the neutral products. The value of the cross section for formation of OH<sup>−</sup> at 5.7 eV is about  $2 \times 10^{-24}$  m<sup>2</sup>. This value is about a factor of four lower than the value ( $8 \times 10^{-24}$  m<sup>2</sup>) estimated by Ref. 2. Tsuda *et al.*<sup>3</sup> did not report the existence of this fragment anion.

### E. CN<sup>−</sup>

The most prominent feature in the CN<sup>−</sup>/C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> ion yield curve (Fig. 3) is an asymmetric resonance located at about 1.5 eV. Such asymmetric resonances with a rather steep slope at the low energy site occur when the Franck–Condon region between the ground state of the neutral molecule and the negative ion state overlap at the dissociative limit. DEA to CN<sup>−</sup>/C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> can proceed via several possible channels, i.e.,



In the present experiment we have no information about the neutral fragments in reaction (7), however, the formation of the CN<sup>−</sup> ion already at low electron energies indicates rearrangement of the bonds in the fragments. From the point of view of energetics, the most favorable neutral fragments are CH<sub>3</sub>O and H<sub>2</sub>O [reaction (7a), CH<sub>3</sub>O can be a hydroxymethyl radical, or a methoxy radical, which is only slightly less favorable]. According to the available data<sup>13</sup> reaction (7a) is exothermic by more than 0.5 eV. Only the channel (7a) can be responsible for the formation of CN<sup>−</sup> at the energies close to zero eV. The next two available channels, (7b) with neutral fragments methanol and OH radical and (7c) with the neutral fragments CH<sub>3</sub>, H<sub>2</sub>O and O are energetically less favorable (they are endothermic by about 0.5 eV and 3.1 eV, respectively). Tsuda *et al.*<sup>3</sup> proposed an additional reaction channel (7d) with an endothermicity of about 5 eV. The channel (7b) could be active at the 1.5 eV resonance. CN<sup>−</sup> is observed also in the electron energy range between 3 and 6 eV, however, with very low ion yield, and therefore we are not able to recognize particular resonances in this interval. Above 6.5 eV a broad structure in the ion yield is observed, peaking at about 8 eV (see the full line in Fig. 3). The positions of the resonances in the CN<sup>−</sup> ion yield are in very good agreement with data published by Jäger and Henglein.<sup>2</sup> The CN<sup>−</sup> ion yield presented by Tsuda *et al.*<sup>3</sup> disagrees totally with the present one and that reported by Ref. 2. The present value of the cross section for the formation of CN<sup>−</sup> via DEA to nitroethane at 1.5 eV is about  $5 \times 10^{-25}$  cm<sup>2</sup>. This value is almost one order of magnitude lower than the value given by Jäger and Henglein.<sup>2</sup>

### F. CNO<sup>−</sup>

The formation of CNO<sup>−</sup>/C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> [Fig. 4(a)] may proceed via the following reactions:



The reactions (8c) and (8d) were proposed by Tsuda *et al.*<sup>3</sup> in order to rationalize resonances at about ~5 eV and ~8 eV. For the very weak signal at low electron energies observed in the present experiment for the first time we propose the additional reactions (8a) and (8b), which are energetically more favorable. According to thermodynamical data in Ref. 13 [ $\Delta_f H_g^\circ(\text{C}_2\text{H}_5\text{NO}_2) = 103 \pm 0.4$  kJ/mol,  $\Delta_f H_g^\circ(\text{CH}_3) = 146 \pm 1$  kJ/mol,  $\Delta_f H_g^\circ(\text{H}_2\text{O}) = -241.83 \pm 0.04$  kJ/mol and  $\text{EA}(\text{CNO}) \sim 3.4\text{--}3.8$  eV] and  $\Delta_f H_g^\circ(\text{CNO}) = 323 \pm 30$  kJ/mol,<sup>1</sup> the energetical threshold for the channel (8a) lies between −0.37 eV (exothermic) and 0.34 eV (endothermic). This channel (8a) could be therefore responsible for the formation of the CNO<sup>−</sup> at low electron energies ~0 eV. Channel (8b) is energetically less favorable with a threshold in the interval 0.64 to 1.19 eV [using  $\Delta_f H_g^\circ(\text{CH}_4) = -74.8$  kJ/mol and  $\Delta_f H_g^\circ(\text{OH}) = 38.99$  kJ/mol], nevertheless, no indication of an opening of this channel at these energies can be seen. At higher electron energies two broad resonances are observed: the first one in the electron energy range from 3 to 7 eV (peaking at about 4.5–5 eV) and the second above 7 eV (maximum at about 8 eV). It is interesting to note that also for other fragment ions a resonance is present in the energy range from 3 to 7 eV, suggesting that these ions are formed via the same intermediate state. The cross section for CNO<sup>−</sup> formation via DEA to nitroethane has a value of about  $3 \times 10^{-25}$  cm<sup>2</sup> and is almost one order of magnitude lower than the value estimated by Jäger and Henglein.<sup>2</sup>

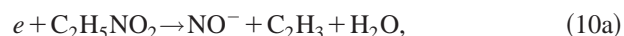
### G. HCN<sup>−</sup>, NO<sup>−</sup>

The weakest product ions in nitroethane are the hydrogen cyanide anion, HCN<sup>−</sup> [Fig. 4(b)] and NO<sup>−</sup> [Fig. 4(c)]. Both are formed in a broad resonance between 3 and 7 eV and NO<sup>−</sup> additionally at 8 eV. Both ions were not observable in nitromethane, even though the HCN and NO cores would be present there.<sup>1</sup> These ions were also not detected in the previous DEA studies to nitroethane.<sup>2,3</sup> The ions could be formed via reactions



Channel (9a) is endothermic by about 2.4 eV and channel (9b) by about 3.7 eV [using  $\Delta_f H_g^\circ(\text{HCN}) = 135.15$  kJ/mol<sup>13</sup> and  $\text{EA}(\text{HCN}) > 1$  eV<sup>13</sup>]. At the resonance observed for HCN<sup>−</sup> both fragmentations channels are energetically allowed.

For the DEA channel NO<sup>−</sup>/C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> the following two fragmentation patterns seem to be energetically most favorable, i.e.,



With  $\Delta_f H_g^\circ(\text{C}_2\text{H}_3) = 299 \pm 5 \text{ kJ/mol}$ ,  $\Delta_f H_g^\circ(\text{C}_2\text{H}_4) = 52.49 \text{ kJ/mol}$  and  $\text{EA}(\text{NO}) = 0.026 \text{ eV}$  (Ref. 13) the thresholds for reaction (8a) and (8b) are 1.64 and 2 eV, respectively. Both channels are thus energetically allowed at the resonances observed in the  $\text{NO}^-/\text{C}_2\text{H}_5\text{NO}_2$  yield located at about 4.5 and 8 eV.

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