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1. Introduction

The project started on April 19, 2001, and already in August 2001, the first successful experiment was carried out at the CRYRING storage ring facility at the Manne Siegbahn Laboratory (MSL), a Swedish national user facility located at the campus of Stockholm University. Considering the fact that MSL is a user facility wit an external program committee that reviews proposals for beam time, the project got a head start. Moreover, the first beam time in August was successful and generated data for two molecular systems, $C_2H_3^+$ and $C_3H_7^+$. Beam time was also granted by MSL for one week in December 2001, and March 2002. Both these weeks were used by the project and were turned into successful experiments. In December, an experiment on $C_2H_5^+$ was carried out, and in March 2002 experiments on $C_2H_4^+$ and C_2H^+.

In September 2001, a female graduate student, Anneli Ehlerding, was recruited to the project, and she has since then worked full time. Also other members of the Molecular Physics Division, apart from the PI and Ehlerding, are involved in the project, but not on a full time basis. The only salary debited to the project is that of Ehlerding, whereas Stockholm University provides the other salaries.

The beam time at CRYRING is free of charge to academic external users with approved beam time proposals, thus no cost for beam time is charged to the project (the beam time cost, if charged, would be about $100K/week).

2. Results

The data analysis for $C_2H_3^+$ is completed, and the paper ha been submitted for clearance and publication; it is accepted for publication in *Astronomy and Astrophysics*. The cross section and branching ratios for dissociative recombination (DR) were measured. The DR rate constant was found to be 5×10^{-7} cm^3s^{-1} at 300 K. The branching ratios measurements showed that 59% of the breakup resulted in three-body formation. The full paper is given in Annex I.
The data analysis for $C_3H_7^+$ is almost completed, and the preliminary branching ratios are given below. The larger number of atoms made the analysis complicated, and the level of detail concerning the branching ratios will be less than for $C_2H_3^+$. Also for $C_3H_7^+$ the three-body breakup channels are significant, which would mean that more radicals are formed than

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Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report results from a contract tasking Stockholm University as follows: CRYRING, a synchrotron/heavy-ion storage ring facility, has proved to be a powerful tool for measurements of branching ratios in recombination of polyatomic molecular ions. However, there are important questions that still need to be addressed for organic ions such as: 1) Is there a mass limit at which fragmentation decreases or even vanishes and most or all of the electron energy is converted to internal degrees of freedom? 2) What is the order, n, of the dissociation shown in reaction? 3) Is the fragmentation process instantaneous? Or is there a delay in the break-up process? For a small inorganic ion such as H2O+ the break-up process is most likely instantaneous, but whether this is also true for larger organic ions is unknown. 4) Is the break-up process a one-step or a multi-step process? Prediction of the products of dissociative recombination is very difficult. It is here proposed to study not only the rates of dissociative recombination of ions important for plasma-enhanced combustion but also the neutral product distributions. Experiments with many important hydrocarbon ions (the benzene cation, for example) will be performed. Another problem concerns the resolution of the solid-state particle detector, because well-resolved mass peaks facilitate the measurement of product branching ratios. Deuterated molecules and peak fitting procedures will be applied to enhance the resolution. The proposed measurements will add greatly to the knowledge base in this unexplored field, yielding answers to the questions outlined above and serving as important inputs to the Air Force combustion models.

15. SUBJECT TERMS
EOARD, Inorganic Chemistry, Physics, Plasma Physics, Combustion, Molecular Chemistry

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assumed in plasma enhanced combustion models. A publication is presently being prepared and a draft manuscript will be ready at the end of the summer 2002.
Concerning the hydrocarbon ions $C_2H_5^+$, $C_2H_4^+$, and C_2H^+ the data are being analyzed, and the results given below should be regarded as preliminary. The results for $C_2H_5^+$ are not yet ready.

$$C_2H^+ + e \rightarrow \begin{cases} C_2 + H & 0.45 \\ CH + C & 0.38 \\ C + C + H & 0.17 \end{cases}$$

$$C_3H_7^+ + e \rightarrow \begin{cases} C_3H_6 + H & 0.42 \\ C_3H_5 + H_2 \\ C_3H_5 + H + H \end{cases} 0.11 \quad \begin{cases} C_3H_4 + H_2 + H & 0.09 \\ (C_3H_3 + H_2 + H_2) \\ (C_2H_6 + CH) \\ (C_2H_5 + CH_2) \end{cases} < 0.05 \quad \begin{cases} C_2H_4 + CH_3 \\ C_2H_4 + CH_2 + H \end{cases} 0.04 \quad \begin{cases} C_2H_3 + CH_4 & 0.19 \\ C_2H_3 + CH_3 + H \\ C_2H_2 + CH_4 + H \\ C_2H_2 + CH_3 + H_2 \end{cases} 0.11$$

$$C_2H_4^+ + e \rightarrow \begin{cases} C_2H_3 + H & 0.03 \\ C_2H_2 + H + H & 0.84 \\ C_2H_2 + H_2 & 0.03 \\ C_2H + H_2 + H & 0.05 \\ CH_4 + C & 0.02 \\ CH_3 + CH & 0.01 \\ CH_2 + CH_2 & 0.02 \end{cases}$$

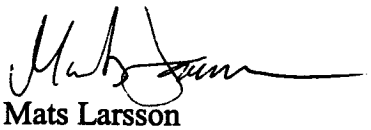
3. Declarations

"The contractor, Stockholm University hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract no. F61775-01-WE035 is complete, accurate, and complies with all requirements of the contract.

DATE: 020626
Name and Title of Authorized Official: _____ "

"I certify that there were no subject inventions to declare as define in FAR 52.227-13, during the performance of this contract"
DATE: 020626
Name and Title of Authorized Official: _____

Sincerely,



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Dissociative recombination of $C_2H_3^+$

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Abstract.

We have studied the vibrationally relaxed $C_2H_3^+$ ion in the' heavy - ion storage ring CRYRING in Stockholm. We measured the dissociative recombination absolute cross section over center-of-mass energies in the range between 0 and 0.1 eV by scanning the electron energy.

The rate of different neutral product channels of dissociative recombination was measured. We found the three-body channel $C_2H + H + H$, with a branching ratio of 59%, to be the dominant one. Finally, we compare $C_2H_3^+$ and $C_2H_2^+$ (Derkatch et al. 1999) results.

Key words. Molecular processes – ISM: molecules – ISM: clouds

1. Introduction

Molecular synthesis within interstellar clouds is governed primarily by ion chemistry (Adams & Smith 1988, Millar et al. 1997, Smith & Spanel 1995). The significant role attributed to ions results from a combination of the low temperatures involved (10-100

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DR were shown to be a significant channel, the models would predict an even greater enhancement due to the plasma.

2. Experiment

The experiment was performed at the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory in Stockholm. The experimental setup and data analysis procedure have been described previously in detail (Strömholm et al. 1996, Neau et al. 2000). Here we only give a brief description and concentrate on issues attributed to the specifics of the present experiment.

Fig. 1 shows the layout of the storage ring. The $C_2H_3^+$ ions are produced in a hot-filament discharge ion source (MINIS). In this ion source it is expected that two isomers of $C_2H_3^+$ can be produced, one is a classical linear structure, and the other is a non-classical bridged form. Fig. 2 illustrates these two isomers (Weber et al. 1976), which are separated in energy by 5 kJ mol^{-1} (0.05 eV). Experiments only start after 4-5 seconds so that an equilibrium mixture is likely. After extraction from the source, the ions are accelerated to 40 keV, passed through a dipole magnet, which serves as a mass separator and then injected into the storage ring. The ring, which has a circumference of c = 51.6 m, consists of twelve straight sections separated by bending magnets. One of the sections is equipped with a radiofrequency acceleration system. The ions are accelerated to the maximum energy of E = 3.56 MeV, which is limited by the magnetic rigidity of the storage ring. After acceleration, the ions periodically penetrate a uniform, average-velocity merged electron beam, which is confined to a diameter of 4 cm by a solenoidal magnetic field over an effective interaction length, l, equal to 85 cm. The electron beam is steered in and out of the interaction region by a couple of toroidal fields. In the present experiment an electron beam with a density of 1.3×10^6 cm^{-3} is used.

The velocity distribution of the electrons in the rest frame of the moving ions is described by a flattened Maxwell distribution characterized by different electron temperatures in the directions parallel, $kT_\parallel$, and transverse, $kT_\perp$, to the ion beam (Danared et al. 1994). The transverse electron beam temperature, being originally as high as $kT_\perp$ = 100 meV (which is determined by the cathode temperature, 1200 K), is reduced to about 2 meV, prior to entering the interaction region by using adiabatic expansion of the electron beam in a decreasing magnetic field (Danared et al. 1998). The longitudinal energy spread of the accelerated electrons is about 0.1 meV. In the interaction region, the heat from the ion beam is transferred to the cold, average-velocity matched, continuously renewed electron beam via Coulomb interactions between the electrons and the ions. It leads to reduction of the momentum spread of the ion beam. As a result, the ion beam, confined by the magnetic fields in the ring, shrinks in diameter. Under such circumstances a typical storage time of the ion-beam is about 10

3. Data analysis

3.1. Dissociative recombination cross section

The measurement is performed after 5 s of cooling time, which is long enough to allow the ions to relax through infrared emission to their vibrational ground state. The DR cross sections are studied over center-of-mass energies ranging between 0 eV and 0.1 eV by scanning the electron energy. First, the cathode voltage is rapidly increased to a specified maximum value and then linearly decreased to the minimum value while crossing the cooling voltage in between. It is possible to study DR reactions at the same center-of-mass energies where the electron beam moves both faster and slower than the ions. The rate at which neutral products of DR reactions are detected, $C_{DR}(t)$, is proportional to the corresponding rate coefficient, $\langle \sigma v \rangle$, which is essentially the cross section averaged over a flattened Maxwellian electron velocity distribution (Danared et al. 1994):

$$\langle \sigma v \rangle = \frac{c}{n_e l} \frac{C_{DR}(t)}{N_i(t)}, \tag{4}$$

where $N_i(t)$ is the number of ions as a function of storage time. The count rate $C_{DR}(t)$ was measured with a single channel analyzer connected to a multichannel scaler. However, it was not possible to resolve the pure DR signal from a background, generated by neutral products of other reactions (collisions of the ions with residual gas molecules), which include at least two carbon atoms. Thus, the high and low discrimination levels in the SCA are chosen to register all pulses with amplitudes characteristic for detection of at least two carbon atoms. Fig. 4 shows both the electron energy scan and the MCS spectrum, which was measured during 2200 injection cycles. A part of the scan, corresponding to high center-of-mass energies at which DR cross sections are negligibly small, gives a direct measure of the collisional background. After its interpolation over the entire scan, the pure DR count rate, $C_{DR}(t)$, is easily derived.

The number of ions circulating in the ring cannot be measured at the same time as the DR signal since this requires a much more intense beam than the silicon detector (exposed from intense flux of DR products) can handle. Therefore, the part of the spectrum which is fully dominated by the background, is also used as an indirect measure of the ion beam intensity. Then, in an independent experiment a count rate of the collisional background, which is measured after turning the electron beam off, is related to the ion current.

The absolute cross sections are obtained after dividing the measured rate coefficient by the detuning velocity, as shown in Fig. 6. Independently, they are derived by unfolding the measured rate coefficient with a numerical Fourier transform (Strömholm et al. 1996). The DR cross sections are corrected for the DR events that occur in the toroidal section of the electron cooler, where non-zero angles between the ion and the electron beams make collision energies different than in the straight section of the electron cooler (Lampert et al. 1996).

4. Results and discussion

4.1. Dissociative recombination cross section

The total cross section for DR of $C_2H_3^+$ is shown in Fig. 6 over a collisional energy range from 10^{-6} to 10^{-1} eV. The total error in the cross section is about 20% at low energies; this limit is based on uncertainties in the ion beam current (15%), the effective length of the electron cooler (7%), and the electron density (7%). Above approximately 1 meV, the data become scattered due to weak signals and a relatively large background signal subtraction. The errors are mainly represented by the scatter in the data, i.e. statistical variations. Errors in the energy are estimated to be 0.5 meV at the lowest collision energies and up to 3 meV at the highest energies. They are mostly attributed to the finite width of the time (energy) windows in the MCS spectra. The cross section decreases rapidly with increasing collision energy and can be represented by a power law with an energy dependence of $E^{-1.36}$. This is larger than the $E^{-1.0}$ dependence applicable to the direct mechanism for DR. The total cross sections are larger than those recently found for $HCNH^+$, and the energy dependence is also larger. Integrating the measured cross sections yields rate constants as a function of translational temperature, the most useful way to represent the data for modeling purposes. The results are shown in Fig. 7. The data are curved on this plot with a break just below 1000 K. The higher translational temperature data follow a $T^{-1.38}$ dependence, and the low temperature data follow a $T^{-0.84}$ dependence being as high as $5 \cdot 10^{-7}$ cm^3s^{-1} at 300K. The break may indicate a change in mechanism.

4.2. Dissociative recombination branching fractions

For dissociative recombination of $C_2H_3^+$, six product channels are energetically accessible (Mallard & Linstrom 2001):

$$
\begin{aligned}
C_2H_3^+ + e \rightarrow \quad & C_2H_2 + H + 6.74 \text{ eV}, && (\alpha),\\
& C_2H + H_2 + 5.59 \text{ eV}, && (\beta),\\
& C_2H + H + H + 1.07 \text{ eV}, && (\gamma),\\
& C_2 + H + H_2 + 0.40 \text{ eV}, && (\delta),\\
& CH_3 + C + 2.39 \text{ eV}, && (\epsilon),\\
& CH_2 + CH + 1.17 \text{ eV}, && (\varepsilon).
\end{aligned}
\tag{6}
$$

Channels α, β, γ and δ involve only C-H bond dissociations, corresponding to the loss of 1-3 hydrogen atoms, while channels ϵ and ε involve C-C bond dissociations. All six channels were found to have a non-zero contribution at a translational energy of near zero; the branching ratios are shown in Table 1.

The C-H bond dissociation channels (α-δ) account for 97% of the total reactivity. Although loss of a single H atom is the most exothermic reaction pathway, the branching

mates the contribution of three-body product channels. The updated model also assumed that C-C bond dissociations would be more significant than had been considered previously. The direct C-C bond dissociation channel was assigned a branching ratio of 0.23. This considerably overestimates the degree to which the carbon skeleton is broken during DR. Compared to the model inputs, the experimental results suggest that DR of $C_2H_3^+$ produces (a) more H atoms, together with less saturated carbon species, and (b) fewer one-carbon species.

In order to investigate how general the $C_2H_3^+$ results may be with regard to DR of other small organic ions, the present results are compared to the recently published results for $C_2H_2^+$ (Derkatch et al. 1999). To facilitate a comparison of the two DR processes, products that result from similar bond cleavages are shown on the same row in Table 1. The $C_2H_2^+$ DR channels that correspond to a loss of one or two H atoms are the most significant product channels, as was also observed for $C_2H_3^+$. However, the relative significance of those channels is reversed for the two molecular ions being considered. Specifically, the two-body dissociation resulting in a loss of only one H atom accounts for 50% of the $C_2H_2^+$ reactivity, compared to only 30% for $C_2H_3^+$, while production of two H atoms accounts for 59% of the $C_2H_3^+$ reactivity, compared to only 30% for $C_2H_2^+$. The smaller two H atom loss associated with the DR of $C_2H_2^+$ is likely a result of energetic considerations. The exothermicities associated with the loss of two H atoms from $C_2H_3^+$ and $C_2H_2^+$ are 1.07 and 0.2 eV, respectively. The smaller exothermicity for $C_2H_2^+$ leads to fewer exothermic phase space channels, which is manifested as a smaller branching ratio. Given the small exothermicity, it is actually somewhat surprising that two H atoms are lost in approximately one third of the $C_2H_2^+$ DR reactions. Loss of two H atoms followed by formation of H_2 is a minor channel for both systems, with branching ratios approximately 7-10% of that associated with the loss of 2 H atoms.

A large difference is noted between $C_2H_2^+$ and $C_2H_3^+$ DR with regard to the C-C bond dissociation channels. Both the direct bond cleavage and the bond cleavage coupled with hydrogen rearrangement channels are at least four times more prevalent for $C_2H_2^+$ than for $C_2H_3^+$ although the exothermicities are the same. The only simple explanation is that the more exothermic C-H bond dissociation channels in $C_2H_3^+$ compete more effectively with the C-C bond dissociation channels, thereby reducing the branching ratios for the latter channels. The competition between C-C and C-H bond dissociations will be explored further with more saturated compounds such as $C_2H_5^+$, where the C-C dissociation channels are also more exothermic.

The $C_2H_3^+$ ion shows a preference for three-body product dissociation, 62% overall, which is approximately twice as much as noted in DR of $C_2H_2^+$. As the comparison between these related species demonstrates, it is difficult at this time to generalize the present results to a wide variety of hydrocarbon ions. Future experiments with hydro-

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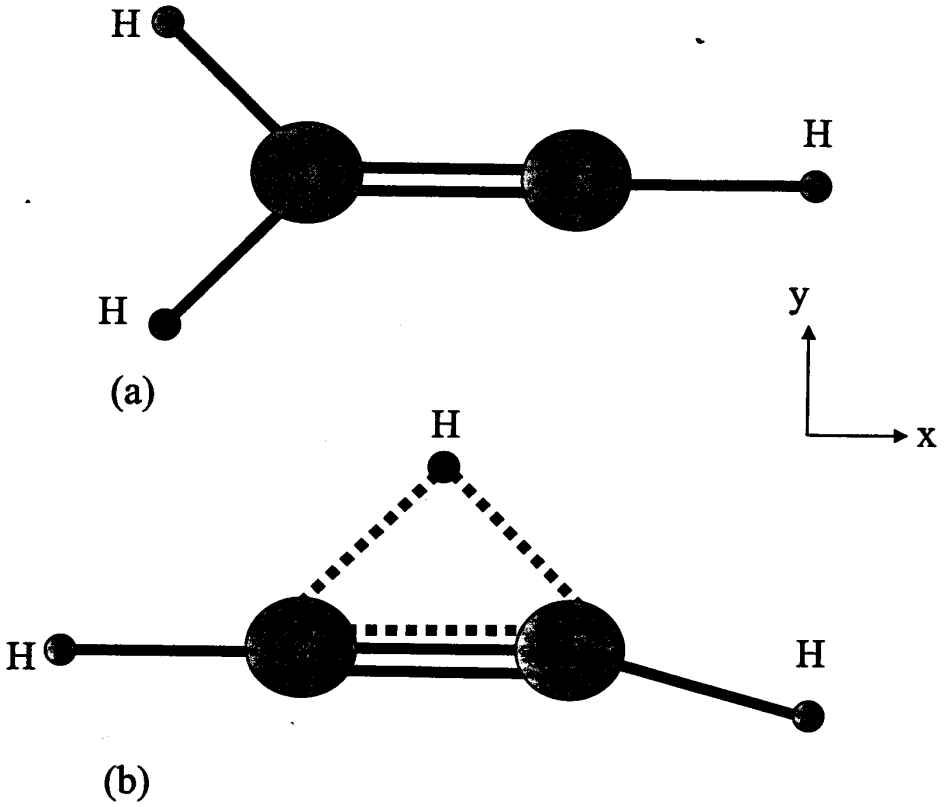

Fig. 2. Molecular structures for vinyl cation $C_2H_3^+$: (a) classical; (b) bridged.

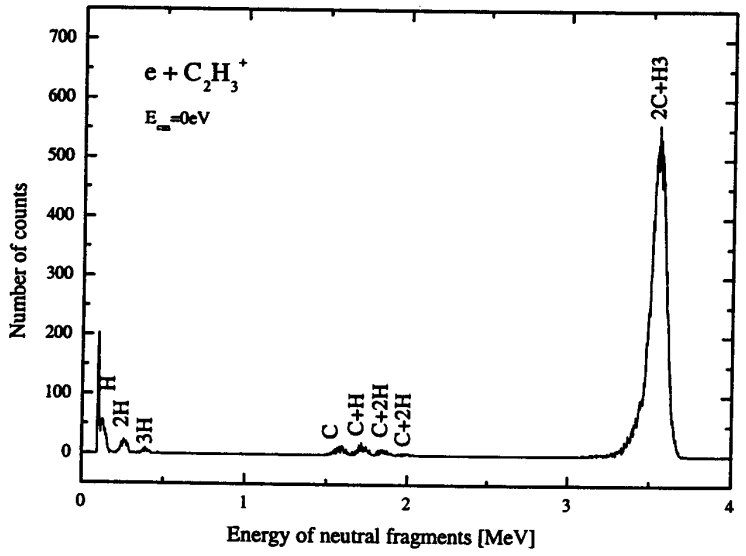

Fig. 3. Energy spectrum of neutral fragments from DR of $C_2H_3^+$ measured at 0 eV collision energy.

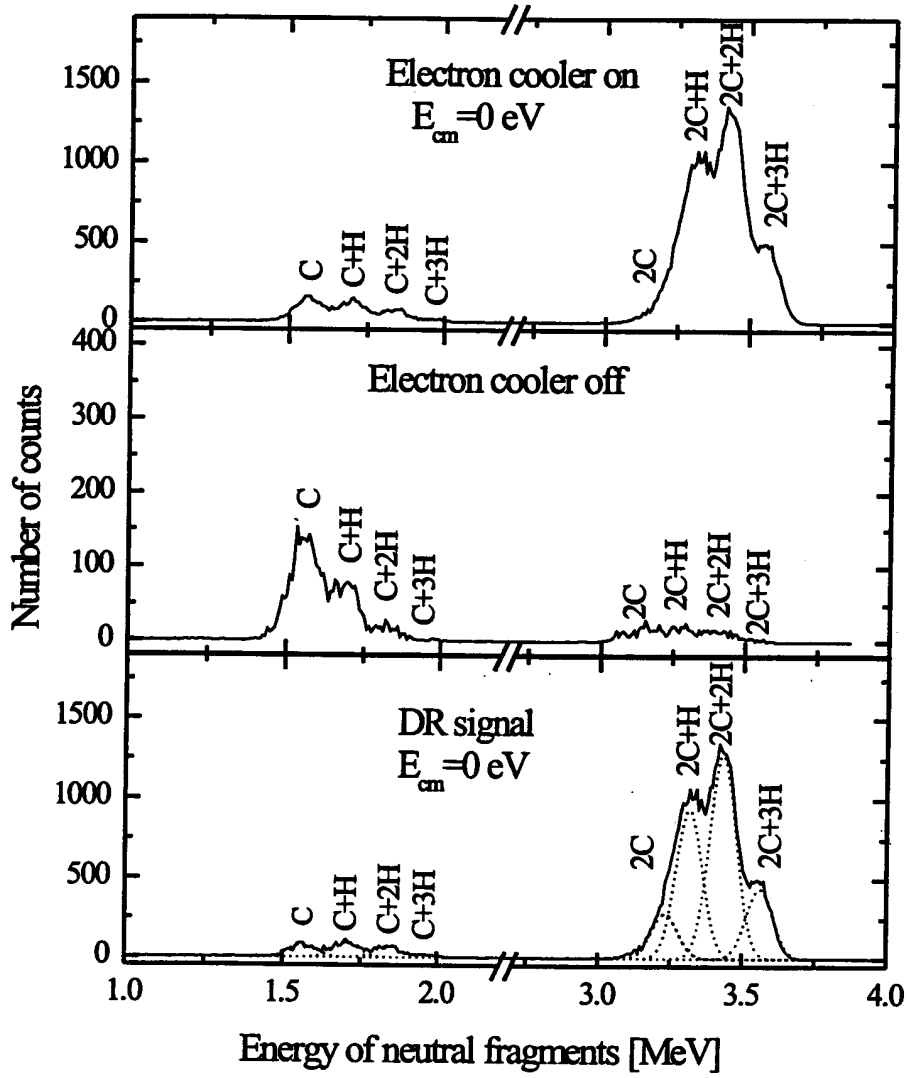

Fig. 5. Energy spectra of neutral fragments from DR of $C_2H_3^+$ measured with a grid in front of the detector. *Top* : Spectrum measured at 0 eV collision energy. *Middle* : Background spectrum measured after turning the electron beam off. *Bottom* : DR spectrum obtained after subtracting the background contribution.