Electron Impact Ionization/Dissociation of Molecules:
Production of Energetic Radical Ions and Anions

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Abstract. In order to provide quantitative information on electron collision processes involving various plasma constituents (in particular hydrocarbons) and to elucidate the properties of cations and anions produced we have carried out the past years a series of studies with a variety of techniques in our laboratory in Innsbruck. In the present review we will present some recent results on electron impact ionization and attachment in order to illustrate recent progress in this field in particular concerning the production of energetic fragment cations for hydrocarbons and differences in the attachment of isomers for nitro-organics. Using a Nier type electron impact ion source in combination with a double focusing sector field mass spectrometer, partial cross sections for electron impact ionization of acetylene, propene and other hydrocarbons have been measured for electron energies up to 1000 eV. Discrimination factors for ions have been determined using the deflection field method in combination with a three-dimensional ion trajectory simulation of ions produced in the ion source. Analysis of the ion yield curves obtained by scanning the deflectors allows the assignment of ions with the same mass-to-charge ratio to specific production channels on the basis of their different kinetic energy distributions. This analysis also allows to determine, besides kinetic energy distributions of fragment ions, partial cross sections differential in kinetic energy. Moreover charge separation reactions (for instance in case of acetylene the Coulomb explosion of the doubly-charged parent ions $C_2H_2^{2+}$ into the fragment ions $C_2H^+$ and $H^+$) are investigated by means of a number of metastable mass spectrometry methods and the associated mean kinetic energy release is deduced. Free electron attachment to the three different isomers of mono-nitrotoluene molecules in the gas phase is studied using two different crossed electron-molecule beams technique. In contrast to previous studies for a large number of negative ions in nitro-organic compounds the presently measured relative cross section curves are recorded with an electron energy resolution of better than 100 meV. For several product anions including the nitro anion $NO_2^-$ remarkable differences for the three isomers are observed. For almost all fragment anion efficiency curves the 2-nitrotoluene exhibits pronounced differences compared to the two other isomers. In contrast, 3- and 4-nitrotoluene disagree only slightly in a few fragment anions from each other.
1. Introduction
Collisions between electrons and atomic or molecular targets (atoms, molecules, clusters, biomolecules, ions) have been the subject of intense experimental and theoretical studies since the early days of atomic collision physics. They are of importance in environments such as laboratory plasmas, as well as planetary and cometary atmospheres [1-4]. They are playing an important role in mass spectrometry, analytical chemistry and radiation science. Besides these volume processes (ionization in gases) also reactions between plasma particles and the corresponding plasma vessel walls are of relevance for controlling and modelling plasma reactors [5]. In order to understand and elucidate the role of these processes in a plasma environment, it is essential to have available detailed and quantitative knowledge on the corresponding elementary reactions proceeding in the volume and at the wall (i.e. plasma wall reactions). Today’s situation in terms of accurate data on these processes is still far from satisfying.

In order to provide quantitative information on collision processes involving various plasma constituents (in particular hydrocarbons) and to elucidate the properties of cations and anions produced we have carried out the past years a series of studies with a variety of techniques in our laboratory in Innsbruck [6], including (i) experimental studies about electron ionization of neutrals and ions and electron attachment to molecules (differential, partial and total cross sections, appearance energies, etc), (ii) theoretical studies about electron ionization of neutrals and ions (cross sections) and (iii) reactive interaction of molecular ions with surfaces (surface induced dissociation, surface induced reactions, charge exchange reactions). In the present review we will present some recent results on subject (i) in order to illustrate recent progress in this field in particular concerning the production of energetic fragment ions.

Dissociative ionization of molecules induced by electron impact is a very important process in many different areas such as low-temperature plasmas, radiation chemistry, and in edge plasmas in fusion reactors [1-4,7-10]. Ionic and neutral fragments produced via dissociative ionization often carry substantial amounts of kinetic energy, and the kinetic energy distribution of a particular fragment determines the energy deposition and the energy transfer pathways in the corresponding media. Thus, the modeling of environments where dissociative ionization processes are important requires knowledge not only of the production efficiency and the nature of fragment ions produced but also of their kinetic energy distribution. Furthermore, different pathways leading to the formation of the same fragment ion may have different threshold energies and different exothermicities. Thus the kinetic energy distribution for a given fragment ion can depend strongly on the electron energy.

Unfortunately, fragment ions that are formed with high kinetic energies are often collected with considerably reduced efficiency (in mass spectrometry). This turn may have a strong influence on the cross section values determined [11-14]. With specially dedicated instruments that were constructed to assure uniform collection efficiency absolute partial and total cross sections have been measured the past years [15,16]. However, with commercial instruments comparable results can only be obtained if the discrimination factor for highly energetic fragment ions is taken into account. For a standard double focusing mass spectrometer equipped with a modified Nier-type ion source we demonstrated some time ago that ion trajectory calculations of the extraction region of this ion source allows the determination of the corresponding ion loss [11]. After correction of the ion efficiency curves with these discrimination factors the agreement with the above mentioned data from the especially dedicated instruments is extremely good. In order to get information on the kinetic energy of the ions (which is a necessary prerequisite for this correction procedure) a deflection method after the ion source was applied in the direction perpendicular to the plane of the mass spectrometer. The present review concerns work carried out as an extension of this earlier method (using an advanced three dimensional ion trajectory simulation) and the kinetic energy distribution of the fragment ions obtained is used to determine for the first time complete sets of ion kinetic energy differential cross sections for these fragment ions. Furthermore, highly energetic ions from hydrocarbon targets such as H+ and H2+ were measured too which was not possible in the earlier study. The determination of the kinetic energy distributions of the fragment ions as a function of the electron energy allows in addition
to distinguish between different ionization processes that lead to the production of a given fragment ion. For instance C$_2$H$^+$ produced via electron impact on acetylene can be formed via neutral H loss from an excited C$_2$H$_2$$^+$ or via Coulomb explosion of C$_2$H$_2$$^{++}$ into C$_2$H$^+$ + H$. Additional studies on the stability of such doubly charged parent ions have been performed using the MIKE method allowing to deduce the kinetic energy release distribution via Coulomb explosion in the metastable time regime. So far measurements on partial and energy-differential cross sections have been carried out in our laboratory for CH$_4$, C$_2$H$_2$, C$_3$H$_4$, and C$_3$H$_6$. Here we will in particular review data on C$_2$H$_2$ and C$_3$H$_6$, for CH$_4$ see Ref. [17] and for C$_3$H$_4$ see a forthcoming paper [18].

Nitro-organic compounds are molecules with a significant potential for the industrial use, particularly as explosives, additives to explosives or propellants [19]. The detection of explosives and their degradation products is a topic of increasing interest in today’s world and dissociative electron attachment (DEA) is one of the more sensitive and specific methods used [20-22]. Moreover, the interaction of electrons with nitro-organic compounds, in particular electron attachment cross sections, plays an important role in understanding the reactivity of these compounds. Therefore, we have some time ago carried out studies concerning DEA to the simple nitro-organic molecules nitro-methane and nitro-ethane [23,24]. These studies have been extended recently to nitrobenzene and nitrotoluenes using a high resolution crossed electron-molecule beams technique [25-28]. In contrast to previous studies for a large number of negative ions relative cross section curves are measured here with an electron energy resolution of better than 100 meV thus giving more insight in the reaction characteristics.

Nitro compounds contain one or more nitro (NO$_2$) functional groups, thus they possess very pronounced electron-acceptor properties due to the low energy of the lowest unoccupied (π*) orbital of the NO$_2$ group. Therefore the interaction between low-energy electrons with nitro derivatives was a subject of many studies. Particularly, nitrobenzene and nitrotoluene were studied rather early by using the swarm technique [29]. The investigators observed nondissociative electron attachment to nitro compounds which form long-lived molecular anions and dissociative electron attachment that produce intense NO$_2^-$ (m/z 46) fragment anions. Furthermore, Harvey et al. [30] demonstrated by measuring the NO$_2^{-}$ resonance energies for 25 different nitro aromatic compounds including several isomeric species that it is possible to distinguish structural isomers of nitro compounds, including the three isomers of mono-nitrotoluene (mono-NT). Although other fragment anions besides the dominant NO$_2^-$ upon DEA to nitro-organic compounds have been detected these product anions have not been investigated concerning the identification of the precursor substance or possible isomeric effects. In our recent study we compared 55 common fragment anions of the three different isomers of mono-NT that could be measured within the detection limit of our instruments [26]. For almost all fragment anions we observe strong deviations of the 2-NT compared to the 3-NT and 4-NT. However, as discussed here in detail the latter two isomers can only be distinguished by the anion efficiency curves of two fragments. Moreover, we have also carried out similar studies for nitrobenzene and di- and tri-nitrotoluene (see Ref. [27,28]).

2. Experimental

2.1. Electron impact ionization studies
The apparatus used for the ionization cross section studies is a double focusing two-sector-field mass spectrometer of reversed geometry with a Nier-type electron-impact ion source (see Fig.1) and has been described in detail in earlier publications [11,31]. A stagnant target gas is crossed by a well-characterized magnetically confined electron beam with a FWHM energy spread of about 0.5 eV. Ions produced by electron impact are extracted from the ion source either by a weak penetrating electric field (typically 50 V/m) or by a strong homogeneous electric field (3 kV/m) generated by a number of electrodes that are part of the front and back side of the ion source interaction region. Ions are then accelerated to 3 kV before entering the analyzing part of the mass spectrometer through a narrow entrance slit, the ions pass two pairs of perpendicular deflection plates that allow the ion beam to be
steered in the y- and z-direction. These deflection plates are used in cross section measurements to sweep the extracted ion beam across the entrance slit [32] and to integrate the detected ion signal. After passing through a magnetic sector field followed by an electric sector field, the ions are detected by a secondary electron multiplier operated in the pulse counting mode.

![Diagram of the experimental setup](image)

**Figure 1:** Schematic view of the experimental setup to measure electron impact ionization cross sections. The two pairs of parallel plates for deflection of the ion beam perpendicularly to the beam direction are designated as deflector plates.

The combined action of the two sector fields in a double focusing mass spectrometer results in a focusing of the ions within the plane of the instrument which corrects for the angular and spatial spreads of the starting points of the ions and for small variations in the kinetic energy. However, the only way to compensate a velocity component outside of the plane of the instrument (z-direction, see Fig. 1) is a corrective action with the so called z-deflector plates right after the ion source. The ion yield, measured as a function of the z-deflection voltage, allows the determination of the kinetic energy distribution for a given fragment ion [11,33]. However, the weak penetrating field that is normally applied cannot extract fragment ions that have initial kinetic energies in the z-direction larger than 100 meV [34]. With the repeller (located in the back of the ion source) and the first lenses that form the front of the interaction region (of the electrons and the neutral molecules), it is possible to generate a strong homogeneous electric field that is able to extract ions with initial kinetic energies up to several eV into the z-direction. This mode of operation has to be chosen to determine the kinetic energy distribution of swift fragment ions.

In the present case of acetylene and propene, decay reactions of dications do not only occur in the ion source immediately after electron impact, but also occur in a metastable time regime. We use the high voltage (HV) scan technique for the measurement of metastable decay reactions of the kind

\[ m_1^{z1+} \rightarrow m_2^{z2+} + m_3^{z3+} \]  

(1)

occurring in the first field free region (ff1) and the mass analyzed ion kinetic energy (MIKE) scan technique in the second field free region (ff2). Beynon and co-workers [35] have shown that the translational kinetic energy release T in the simple charge separation reaction (1) can be calculated...
from the corrected (i.e., for the width of the precursor ion peak) width of the metastable peaks $\Delta U$ and $\Delta E$ using the relations

$$T = \frac{z_1^2 m_1^2 U_0}{16 z_2 m_1 m_3} \left( \frac{\Delta U}{U_0} \right)^2$$

(2)

$$T = \frac{z_1^2 m_1^2 U_0}{16 z_2 m_1 m_3} \left( \frac{\Delta E}{E_0} \right)^2$$

(3)

where $z_1$ and $m_1$ are the charge state and mass of the precursor ion, $z_2$ and $m_2$ are the charge state and mass of the detected fragment ion, $m_3$ is the mass of the undetected fragment ion, $U_0$ is the acceleration voltage and $E_0$ is the sector field voltage required for the detection of the precursor ion.

2.2. Electron attachment studies

The experiments described below were performed in a crossed electron/molecule beams device (see Fig.2) which has previously been described in detail [36]. In brief, the electron beam is formed in a custom built hemispherical electron monochromator, operated at an energy resolution between 60 and 120 meV (FWHM) and an electron current of 5-20 nA. 2-NT and 3-NT are under standard condition liquids with the vapor pressure sufficiently high for the present experiment. 4-NT forms yellow crystals and requires moderate heating of the gas inlet system to about 40°C to obtain the same target density of 2×10$^{-4}$ Pa (as for 2-NT and 3-NT) in the ion source measured by a hot cathode ionization gauge. The samples used are obtained from Sigma Aldrich with a stated isomeric purity of >99% for the 2-NT and >98.5% for the 3-NT and 4-NT. An effusive molecular beam is formed by introducing the molecules through a capillary (diameter of about 0.8mm) which is located in front of the ion source. The electron beam is crossing the molecular beam in the reaction chamber. Negative ions formed in the crossed beams collision zone are extracted by a weak electric field towards the entrance of the quadrupole mass spectrometer. The mass-selected negative ions are detected by a channeltron using a single pulse counting technique. The intensity of a particular mass-selected negative ion is then recorded as a function of the electron energy. The electron energy scale is calibrated using the well known SF$_6^-$ signal from SF$_6$ or the Cl$^-$ from CCl$_4$ signal which exhibit narrow s-wave resonances at 0eV. The apparent width of the resonance is used as a measure for the electron energy resolution of the electron beam. In some cases we have used instead of this monochromator machine, the apparatus described above employing a double focusing two-sector field mass spectrometer equipped with a standard Nier-type ion source. In this case the electron energy resolution close to 0 eV is about 1 eV at a regulated electron current of about 10 µA at 2 eV thus allowing a much wider dynamic range in ion detection with less discrimination for kinetic fragment anions than in the monochromator machine.

3. Results

3.1. Ionization cross sections and decay reactions of acetylene and propene

Fig.3 gives a mass spectrum of acetylene ionized by 100eV electrons (see also Ref.[37] for more detail). This mass spectrum is corrected for the residual background and the discrimination effects due to the initial kinetic energies of the ions. Also shown in this figure are the two isotopomers $^{13}$C$^{12}$CH$_2^+$.
and $^{13}$C$^{12}$CH$_2$ which have an abundance of about 2 % of the main isotope peaks, respectively. Since the $^{13}$C$^{12}$CH$_2^{++}$ ions appear at the non-integer mass-to-charge ratio of 13.5 amu, this peak can be assigned unambiguously to the doubly-charged acetylene ion, whereas the peak at mass 13 consists of both ions, e.g., $^{13}$C$_2$H$_5^{++}$ and $^{13}$CH$^+$. The z-profiles of the mass to charge ratio of 13 amu in Fig. 4 exhibit a strong increase of the low-kinetic energy contribution at electron energies above 36 eV (this is the ionization energy measured here for the appearance of $^{13}$C$^{12}$CH$_2^{++}$ at 13.5 amu). Therefore, these ions with thermal kinetic energies are attributed to dication because no kinetic energy release is involved in the ionization process for these parent ions.

In order to elucidate this behaviour of the z-profiles, we analyzed these beam profiles in a more quantitative way (for details see Ref. [34]), i.e., the initial ion kinetic energy distribution and the extraction efficiency (discrimination factor) from the ion source for a given product ion are determined by fitting measured ion beam z-profiles with a superposition of simulated ion beam profiles. Note that in the earlier method described by Poll et al. [11] the measured z-profiles are assumed to be unaffected by reduced extraction efficiency. In contrast the present method of fitting a weighted superposition of 3-D simulated z-profiles to the experimental data allows the analysis of ion beam profiles of highly energetic fragment ions that are affected by the reduced ion extraction efficiency. The output of the fitting procedure is a kinetic energy distribution (see results given for fragment ions at mass 13 shown in Fig.5) and a corresponding discrimination factor for each fragment ion at each electron energy considered. The discrimination factors are a measure for the loss (due to their kinetic energy) during the extraction procedure of the ions produced in the ion source. The kinetic energy distributions obtained for the fragments with m/z ratios 13 reveal a pronounced dependence on the electron energy.

Multiplication of the measured apparent partial ionization cross sections with the corresponding discrimination factors provides a compensation for the reduced extraction efficiency, thus yielding accurate partial cross sections with the present experimental set-up [37]. Although the kinetic energy distribution functions can differ slightly depending on the starting parameters in the calculations, the results for the discrimination factors are independent of these variations. Depending on the kinetic energy of the fragment ion (which depends on the incident electron energy), the values of the discrimination factors lie between 1.058 for the parent ion (which does not show any dependence on incident electron energy) and 2.12 for the C$_2$H$^+$ ion at 200 eV incident electron energy. The corrected absolute partial cross sections for the fragments C$_2$H$_2^+$, C$_2$H$^+$, C$_2^+$, C$^+$, CH$_2^+$ and CH$^+$ are summarized.
Figure 3: Mass spectrum of acetylene measured with an electron energy of 100 eV and an electron current of 370 µA (corrected for background contributions and for discrimination effects, see text).

Figure 4: Ion yield profiles (z-profiles) of the CH⁺ ion.

in Fig. 6. Absolute cross sections were obtained in this case by normalizing the sum of these partial cross sections at each electron energy with the corresponding absolute total cross sections obtained by Tian and Vidal [38]. Error bars for the partial cross sections before normalization with the data of [38] are estimated to lie within 15%. Within these error bars there is good agreement between the present partial cross section data and those of Tian and Vidal [38], except for C⁺ where the present cross sections are smaller by a factor of 2. It is interesting to note that the earlier data of Zheng et al. [39] (which did not take into account discrimination effects) are for all ions formed smaller than the present ones and those of Tian and Vidal [38].
Cross section curves that are differential with respect to the kinetic energy of the ion can be deduced from the kinetic energy distributions and the partial cross sections (see for details Ref. [17]). The energy distribution function for the CH⁺ is divided into two parts: The range of the initial kinetic energy between 0 and 0.5 eV we call the thermal or low energy regime and initial kinetic energies higher than 0.5 eV are the high energy regime. Figure 7 shows the absolute partial cross section curve of ions with the mass-to-charge ratio of 13 amu (squares) and the separation of this curve into a low (0-0.5 eV, circles) and a high (0.5-10 eV, triangles) kinetic energy part. The curve of the ions with a low kinetic energy has a threshold of about 36 eV which corresponds to the measured ionization energy of $^{13}\text{C}^{12}\text{CH}_2^{++}$. Ionization of $\text{C}_2\text{H}_2$ resulting in $\text{C}_2\text{H}_2^{++}$ does not change the momentum of the resulting ion and the z-profiles of doubly charged parent ions are therefore narrow. Thus we can assign the low kinetic energy part of the cross section at a mass to charge ratio of 13 amu to the formation of $^{12}\text{C}_2\text{H}_2^{++}$, whereas the high energy part is due to production of the fragment ions CH⁺. Similar results can be obtained for the other fragment ions, sometimes allowing to distinguish between formation of the ions via different excitation channels.
Figure 6: Absolute partial cross sections for the fragment ions C₂H₂⁺, C₂H⁺, C⁺, CH₂⁺, and CH⁺ via electron impact ionization of acetylene compared with cross sections obtained by Tian and Vidal [38] and Zheng et al. [39].
Figure 7: Absolute partial cross section curve for ions at mass to charge ratio 13 amu (squares) and cross section curves for this mass per charge ratio that are differential with respect to the kinetic energy. Triangles designate the signal which is coming from ions with high kinetic energy (0.55eV – 10eV) and circles designate the ion yield coming from ions with rather low kinetic energies (0eV – 0.5eV). At around 40eV we can see a strong increase in the slope of the low energy curve which marks the production of the doubly charged parent ion C$_2$H$_2^{2+}$ also present at this mass to charge ratio.

Additional studies on the stability of the doubly charged parent ions have been performed [37]. In case of acetylene we observe a metastable decay reaction of the dicationic parent ion into C$_2$H$^+$ + H$^+$. An analysis of the corresponding MIKE peak shape provides an average kinetic energy release $<\text{KER}>$ of 3.88 eV. Momentum conservation implies a kinetic energy for the heavier fragment ion C$_2$H$^+$ of about 0.2 eV. Moreover, besides this MIKE measurement, we also have determined the metastable fraction [C$_2$H$_2^{2+}$]/[C$_2$H$^+$] as a function of the time after formation of the parent ion C$_2$H$_2^{2+}$ in the ion source. These measurements have been performed with a recently constructed three sector field instrument [40] which enables us to investigate metastable decay reactions in three different field free regions corresponding to three different time windows. By additionally changing the acceleration voltage from 3 kV down to 2 kV the time range can even be expanded. A linear dependence of measured metastable fractions in a semi-logarithmic plot corresponds to a single lifetime. It turns out that the present data are not following a single-exponential curve but correspond to a double-exponential curve. By fitting the curve with a second order exponential fit we deduce a lifetime of 0.3 µs for a fast decay channel and 7.3 µs for a second process.

A similar case has been encountered in case of electron impact ionization of propene [41], i.e. the occurrence of a decay reaction C$_3$H$_5^{2+}$ $\rightarrow$ C$_2$H$_3^+$ + CH$_3^+$ (see also the same decay for dications produced by electron impact ionization of propane [42]) where both singly charged fragments have been observed to exhibit a threshold of about 30 eV above which ions with high kinetic energy are observed. To further elucidate this point we have investigated the stability of the dication C$_3$H$_5^{2+}$ with help of the high voltage scan HV technique and the MIKE scan technique (Fig. 8). An analysis of the peaks allows to deduce a mean kinetic energy release for the Coulomb explosion reaction of about $<\text{KER}> = 5.5 \pm 0.5$ eV for the decay in ff2 (MIKE-scan) and 4.85 $\pm$ 0.5 eV for the decay in ff1 (HV-scan). These results are in good agreement with the estimation of this energy yielding 5.14 eV just by using equation $<\text{KER}> = 14.39/R$ with R equal 2.8Å (the distance between the charges; C=C bond
1.3Å; C-C bond 1.5Å) and assuming that the charges are located at the C atoms at the ends of the chain. Another way to obtain an estimation for this mean kinetic energy release for the Coulomb explosion of the C₃H₅⁺⁺ is to calculate the energy release from the z profiles in the centre of mass system. The value thus obtained, 4.99 ± 0.5 eV, agrees quite well with the mean kinetic energy that we have deduced with the help of the MIKE technique or the HV-scan technique.

Figure 8: MIKE-scan for the decay reaction C₃H₅⁺⁺ → C₂H₂⁺ + CH₃⁺ (induced by electron impact ionization of propene) in the second field free region.

3.2. Electron attachment to isomers of mononitrotoluene

Negative ion mass spectra of the three mononitrotoluene isomers (for more detail see Ref. [26]) obtained by electron attachment at electron energies close to zero eV were measured with the electron monochromator instrument. All mass spectra close to zero eV are dominated by the parent molecular ions M⁻ (m/z=137). However, there exist differences between the isomers in the intensities of the M⁻ ions. The strongest intensity is observed for the 4-nitro-toluene. The mass spectra indicate that the intensity of the M⁻ ion is decreasing as the distance between the methyl and the nitro group is decreasing in the isomers. The fragmentation at 0 eV is strongest for 4-NT where relatively intense fragments with m/z=117, 119 and 121 are present in the mass spectrum. NO₂⁻ anion formation at 0 eV is observed intensely for 2-NT, much less for 3-NT and not at all for 4-NT. CN⁻ formation is only observed for 3-NT close to 0 eV.

In contrast, the negative ion mass spectra measured with the sector field instrument at the electron energy of 4 eV (Figure 9) show strong fragmentation for all isomers. At this electron energy most of the fragment anions show their maximum intensity. For 2-NT 78 fragment anions can be observed whereas for 3-NT and 4-NT only 66 and 55 fragments, respectively, can be identified within the detection limit of the instrument. The strongest ion by far, present in the mass spectra of all isomers, is m/z=46, which corresponds to NO₂⁻. This anion is effectively formed upon DEA to many nitro-compounds. All three mass spectra show several groups of negative ions formed upon DEA to mononitrotoluene, i.e., around m/z=136, 120, 107, 89, 76, 65, 46, 26 and 17. Especially the fragment groups at 65, 76 and 89 amu are much more pronounced for 2-NT. Furthermore, the most intense fragment anion of the 120 amu group is m/z=118 for 2-NT and 3-NT but m/z=120 for 4-NT. The relative
Figure 9: Negative ion mass spectra of the three mono-nitrotoluene isomers recorded at the electron energy of 4 eV and measured with the sector field mass spectrometer. The electron current was set to 10µA and the pressure in the ion source was 2×10⁻⁴ Pa. The three diagrams show the mass spectra from m/z=14 to m/z=140. A logarithmic scale is chosen for the ion yield to compare the mass spectra for the three isomers in a wider range of intensities.

The abundance of m/z=120 is almost an order of magnitude more intense for 4-NT as compared to the other two isomers. Already this quick glimpse at the mass spectra shows significant differences between these three isomers which are even more pronounced when looking at the attachment cross section curves, some of which are given in Fig. 10.

Figure 10 shows anion efficiency curves for three product anions where distinct differences between the three isomers can be observed. The ion yield is normalized to the ion yield of the mass spectra obtained with the sector field mass spectrometer and thus can be compared directly. The metastable molecular anions M⁻ at m/z=137 (not shown in Fig.10) show intense narrow peaks at zero energy for all three NT isomers. The width of this resonance is basically determined by the electron energy distribution of the monochromator instrument used in these parent anion measurements and is about 100 meV for 3-NT and 4-NT and 60 meV for 2-NT. The present experiment is carried out under truly single collision conditions and thus collisional stabilization of the M⁻ is impossible. Thus the observation of the M⁻ ion indicates the long lifetime of this transient negative ions at the microsecond scale (the autodetachment lifetime of these ions is determined with 47±2 µs for all three isomers) which is close to the flight time of the ions from the reaction chamber to the detector of the sector field instrument. Besides the well pronounced peak at 0 eV a very weak shoulder is observed at about 0.45 eV. The drastic intensity reduction of the latter (with respect to the first peak) indicates that the lifetime of the anionic state associated with the second structure is barely sufficient for detection through the quadrupole mass filter, where the required lifetime is in the order of 100µs. The non-dissociative electron capture by 2-NT and 3-NT and the measurement of autodetachment lifetimes of these molecules was already observed by Christophorou et al. [29].

The dominant fragment anion formed via DEA to all isomers of mono-nitrotoluene is the nitrogen dioxide anion NO₂⁻. As can be seen from Fig.10 the NO₂⁻ ion yield for all three isomers exhibits two strong maxima at about 1.4 eV and 3.85 eV and two weak resonances at 6.5 eV and 9 eV. The high
energy features are clearly less pronounced for 2-NT which in contrast to the other isomers shows a narrow 0 eV resonance. The ion yield for m/z=45 is more than 3 orders of magnitude less intense than for the neighboring anion NO$_2^–$. All isomers show a resonance at 3.8 eV and only 2-NT shows an additional resonance at higher energies, i.e., at 8.8 eV. Also the anion with m/z=77 – where both functional groups of the benzene ring are removed and a hydrogen atom of the methyl group binds to the ring – shows for the 4-NT isomer besides the common 4 eV resonance two additional resonances at higher electron energies, i.e., at 7eV and at 10.7eV. 3-NT shows at the high energy side of the 4eV resonance a wide tail. In contrast 2-NT shows a low intensity resonance at 1.5eV. From the electron transmission spectroscopy (ETS) study of nitro derivatives in the gas phase the first peak is associated with simple electron capture into the π* orbital (which has antibonding character between the nitro group and the ring), whereas signals at higher energies are associated with core-excited resonances [43]. It is interesting to note that the position of all resonances for NO$_2^–$ and the complementary anion formed via neutral NO$_2$ loss, i.e. (M-NO$_2$)$^–$ match almost perfectly for all three isomers. This indicates that m/z=91 indeed is the result of a single C-N bond cleavage and loss of a neutral NO$_2$ unit.

![Figure 10: Anion efficiency curves for three fragment anions produced via electron attachment to the three isomers of mono-nitrotoluene. For m/z=77 (top panel) only for 2-NT the monochromator instrument is utilized (thin solid line). However, the low electron energy data obtained with the high mass resolution sector field instrument show exactly the same resonances with even the same relative abundances (thick solid line). The ion efficiency curves for 2-NT are multiplied with 0.2 for better comparison with the other isomers. Anion efficiency curves for the negative ions NO$_2^–$ (middle panel) and mass 45 (lower panel) formed via DEA to the three isomers of mono-nitrotoluene are measured with the high energy resolution monochromator instrument.](image)

It is interesting to note that very recently Harvey et al. [30] using an apparatus with an electron energy resolution of ±300 meV demonstrated by measuring the NO$_2^–$ resonance energies for 25 different nitro aromatic compounds including several isomeric species that it is possible to distinguish structural isomers of nitro compounds, including the three isomers of mono-nitrotoluene. In extension
to the study by Harvey et al. the present work clearly demonstrates that DEA is a suitable tool to
distinguish different isomeric forms of nitrotoluene. In the literature this has been only demonstrated
for the NO$_2^-$ fragment. With this anion it is very easy to distinguish 2-NT from the two other isomeric
forms, however, 3-NT and 4-NT differ only slightly with respect to the relative abundances of the
resonances. For several other fragment anions we observe much more pronounced differences in the
anion efficiency curves for the isomeric forms of nitrotoluene that offer the possibility to distinguish
also easily between 3-NT and 4-NT. 4-NT is the only isomer that exhibits an intense resonance at
electron energies higher than 6 eV for the fragments with m/z=77 (see Fig.10) and m/z=88. We
therefore suggest measuring the mass 46 (or 107) at 1 eV to deduce the yield of 2-NT and the mass 77
at 7eV (or 120 at 4 eV) to determine the amount of 4-NT. From a final measurements of the mass 46 at
4eV the amount of 3-NT can be estimated by subtracting the previously determined yield of 2-NT and
4-NT.

Work partially supported by the FWF, Wien, Austria and the European Commission, Brussels, EU.

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