Hydrogen loss in aminobutanoic acid isomers by the σ ∗ resonance formed in electron capture

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Abstract. The mechanism of a hydrogen loss reaction upon dissociative electron attachment to organic acids and amino acids has been a matter of controversy. In this study, we investigate this process for three isomers of aminobutanoic acid and the deuterated analogue of the α isomer (αA D) in the electron energy range 0–2.5 eV. We implement the resonant R-matrix theory, applying a one-dimensional model involving electron capture into the σ ∗(OH) orbital which reproduces convincingly the conspicuous features of the experimental cross sections, i.e. the pronounced cusps at the vibrational excitation threshold, the substantially different shapes of the three constitutional isomers and the characteristic differences between αA and its isotopologue αA D.
1. Introduction

The loss of an H atom driven by electrons with low energy (nearly 1 eV) is a reaction common to many biologically relevant molecules, including DNA nucleobases [1–5], organic acids [6, 7] and amino acids [8–14]. More generally, low-energy electron (LEE)-driven reactions are considered to be important initial and decisive steps in the molecular description of radiation damage to biological systems. When high-energy radiation (particles or photons) interacts with a biological medium, it is not the direct and primary interaction of the high-energy quanta which causes damage, but rather a variety of reactive intermediates formed within nanoscopic volumes along the energy track. Due to energy and momentum conservation, a high-energy photon will in the first step remove electrons within the molecular network of the cell components, thus leading to various ionization/dissociation channels that are indeed responsible for the production of damaging radicals. Such radicals can, in turn, act on the cell material, thereby becoming the primary cause of cell apoptosis processes [15, 16]. At the same time, the primary photon impact produces a large number of secondary electrons having initial energies in the range of a few tens of eV [17]. Within picoseconds, these ballistic electrons are slowed down by inelastic scattering events (including further ionization processes) until they become bound as solvated electrons and then as chemically rather inactive species.

The particular relevance of LEEs became directly evident after a series of landmark experiments [18–20] in which plasmid DNA was irradiated by a well-defined electron beam at variable energy, resulting in single strand breaks and double strand breaks. Most remarkably, strand breaks were also observed in the energy range below the ionization threshold, with the efficiency showing a resonant behavior with respect to the electron energy. In addition, in the energy range below electronic excitation (<3 eV), single strand breaks were also detected within a structured resonance feature [19]. These were unexpected observations since the traditional notion was that only electrons at energies above the ionization threshold could contribute to DNA damage. From the resonant structure of the damage profile it was proposed that resonant electron captures could occur at particular molecular components and sites of the DNA and thus may be the initial step towards the observed strand breaks. These experiments initiated much activity towards a detailed investigation of the interaction of LEEs with biomolecular systems including the building blocks of DNA, organic acids and amino acids. From gas phase experiments, it was found that all the nucleobases (thymine, adenine, cytosine, guanine
and uracil) [1–5], organic acids [6, 7] and also amino acids [8–14] exhibit a low-energy decomposition reaction triggered by electrons at subexcitation energies (nearly 1 eV), namely dissociative electron attachment (DEA) leading to the loss of a neutral hydrogen atom:

$$e^- + M \rightarrow M^- \rightarrow (M-H)^- + H,$$

where $M^-$ denotes the transitory negative ion (TNI) generated by resonant electron capture and $(M-H)^-$ the closed shell anion formed by the ejection of a neutral hydrogen radical from the TNI.

Amino acids represent building blocks for proteins which are vital components of a living cell. Cells have designed particular proteins that, e.g., specifically bind to single stranded DNA in the course of replication with particular functions [21]. In the light of that, the interaction of LEEs with amino acids is of great significance for the description of the molecular mechanisms in radiation damage. In this paper, we extend the study of H loss triggered by LEEs to the three isomers of aminobutanoic acid ($\alpha$A, $\beta$A and $\gamma$A) and also the deuterated form of $\alpha$-aminobutanoic acid ($\alpha$A$_D$, deuterated at the O and N positions); $\alpha$-, $\beta$- and $\gamma$- refer to the positions of the amino group ($-\text{NH}_2$) in the carbon chain. Schematics of molecular structures of these three isomers are shown in figure 1. Although these three molecules are not building blocks of proteins, they belong to the class of amino acids, and the $\gamma$-isomer, also known as GABA, is an important inhibitory neurotransmitter in the human brain. It inhibits the action of the most important transmitter glutamic acid.

In the simplest organic molecule containing a carboxyl group, formic acid (HCOOH), isotope labeling experiments using HCOOD and DCOOH have in fact shown that H loss exclusively occurs at the OH site [7], which turned out to be the case also for small amino acids [8–14]. In a theoretical study [22], H loss from formic acid (HCOOH) has been attributed to initial electron attachment into the COOH $\pi^*$ MO, followed by out-of-plane distortions, thereby coupling the $\pi^*$ MO, to the $\sigma^*$ MO, ultimately generating HCOO$^-$ + H. In a recent $R$-matrix study [23], the DEA cross section curves were explicitly calculated for both formic acid and glycine using a one-dimensional (1D) model invoking a single $\sigma^*$ valence anion state in which the excess electron is largely localized on the O–H bond. Surprisingly, good agreement with the experimental results could be obtained by taking some kind of extreme properties of the $\sigma^*$ state, namely a resonance energy of 5.5 eV and a width of 5.8 eV. Sharp structures in the experimental cross sections are very well reproduced in the calculated cross section and interpreted as cusps at the vibrational excitation thresholds. More recent DEA studies on glycine [11, 12], serine [13] and formic acid [24] also showed clear structures in the relative cross section at the positions of the $\nu = 3$, 4 and 5 (OH) vibrations in the $(M-H)^-$ yield and further support the role of the $\sigma^*$MO in the dissociative process.
In this paper, we show that this rather simple 1D model with electron capture into the \(\sigma^*(\text{OH})\) can reproduce the main features of the quite different experimental cross section curves of \(\alpha-, \beta-\) and \(\gamma\)-aminobutanoic acid very well.

2. Experiment

The present investigation was performed with a crossed electron/molecular beams device at the Innsbruck laboratory, as described in detail in [25]. The electron beam is formed in a custom-built hemispherical electron monochromator, operated at an energy resolution of about 80 meV (full-width at half-maximum (FWHM)) and an electron current of 5–8 nA. The molecular beam containing the amino acids emanates from a source consisting of a temperature-regulated oven and a capillary. Experiments were performed at 400 K, resulting in sufficient pressure to form an effusive beam of the corresponding amino acid. Negative ions formed in the collision zone are extracted by a weak electric field toward the entrance of a quadrupole mass spectrometer. The mass-selected negative ions are detected by a channel electron multiplier 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 \(\text{SF}_6^–\) signal near 0 eV. The compounds were purchased from Sigma-Aldrich (stated purity of 99.5%). Isotope labeling is performed by successive solvation and distillation cycles with heavy water. From electron ionization mass spectra, we estimate the purity of \(\alpha\text{-A}_D\) to be 99%.

3. Theory

We assume that the low-energy DEA to amino acids considered in this paper is driven by a \(\sigma^*\) resonance. This mechanism is similar to that for hydrogen halides [26] and was discussed in detail in [23]. Recent measurements by Kubala et al [24] confirmed this mechanism for the formic acid molecule.

Due to the complexity of the electron structure of amino acids, \textit{ab initio} calculations of the resonance properties of these compounds (i.e. resonance position and width) present a big challenge. In addition, because the \(\sigma^*\) resonance is very broad, DEA calculations require a nonlocal approach [27]. This means that the resonance width and shift due to interaction with the electron continuum should be calculated as functions of electron energy for a series of nuclear geometries. These data should be used then to calculate the nuclear dynamics in the nonlocal complex potential [27]. An equivalent approach uses the \(R\)-matrix formulations [28], and was applied in previous calculations of DEA to formic acid and glycine [23] and uracil [29].

With all these complications, we attempt a model approach in this paper. We assume that all basic \(\sigma^*\) resonant features in the present compounds are due to the carboxyl group; therefore they can be described by our model for formic acid [23].

On the other hand, since the threshold structures are strongly influenced by the long-range electron–molecule interaction, we modify our model by incorporating proper values of the molecular dipole moment and polarizability. These were calculated using the program GAMESS [30, 31] with the built-in 6-31G(d) AO basis on the principal rotamer. The resulting values of the dipole moment and averaged polarizability are presented in table 1. Our previous calculations for uracil [29] showed that the polarization anisotropy virtually does not affect the...
Table 1. Dipole moment, polarizability (both quantities in a.u.) and reaction threshold (in eV) calculated for the three isomers of aminobutanoic acid.

|     | $\alpha$ | $\beta$ | $\gamma$ |
|-----|----------|---------|-----------|
| Dipole moment | 0.5307   | 0.8059  | 0.7076    |
| Polarizability | 49.86    | 50.17   | 50.25     |
| Threshold     | 1.15     | 1.19    | 1.33      |

DEA cross section; therefore only the isotropic part of the polarization potential was used in the present calculations.

The obtained values of the dipole moment and polarizability were used for the calculation of electron wave functions in different vibrational channels and corresponding attachment amplitudes, as described in [28]. Two models for DEA calculations for formic acid were used in [23]. One parameterizes the $R$-matrix surface amplitude as a function of internuclear distance by an equation containing an exponential function and the other by an equation containing a linear function. The resulting amplitudes are close to each other. However, the $R$-matrix surface amplitude determines the resonance width function, and the threshold DEA cross sections are very sensitive to the latter. Therefore the two calculations produce cross sections of quite different shapes. Although the present calculations employ the first (exponential) model, which was more successful in reproducing experimental results for formic acid, we also give an example of the application of the linear model. It shows that by varying the input parameters for nuclear dynamics calculation within a very narrow range, we can reproduce the experimental data. On the other hand, due to the very high sensitivity of DEA cross sections to these parameters, it would be a very challenging task to achieve agreement between completely \textit{ab initio} calculations and the experiment.

The asymptote of the anion potential curve is also adjusted to satisfy the thermodynamic threshold of the three different isomers. A representation of the neutral and anion surfaces as a function of the O–H (or O–D) distance relative to equilibrium is shown in figure 2. The vibrational energy levels are shown by horizontal lines; a value of 0.437 eV was used for the fundamental O–H stretch vibration $\nu_{\text{OH}} = 0 \rightarrow 1$, and 0.314 eV for $\nu_{\text{OD}} = 0 \rightarrow 1$. The thermodynamic threshold or the reaction enthalpy ($\Delta H_0$) for the hydrogen loss reaction can be expressed as

$$
\Delta H_0 = D(\text{O–H}) - \text{EA}(\text{M–H}),
$$

with $D$ being the bond dissociation enthalpy of the (O–H) bond and $\text{EA}$ the electron affinity of the radical (M–H). Since the particular electron affinities and the specific O–H binding enthalpies are not available, we have calculated these quantities by applying \textit{ab initio} quantum chemical calculations using the G4(MP2) method [32]. This extrapolation scheme uses various basis sets and levels of theory to obtain accurate values of thermochemical properties. The $\Delta H_0$ values include the zero-point vibrational energies and thermal corrections at room temperature. The calculations were performed with the Gaussian 09 computer code [33]. The reaction threshold is extracted from the difference between the products (H + RCOO$^-$) minus the parent ground-state energies. The calculated values are reported in table 1 and have an accuracy of about 0.15 eV.
Figure 2. Potential energy curves as a function of the O–H separation relative to the equilibrium for α-aminobutanoic acid. Horizontal lines indicate the energy levels of OH stretching vibration (solid line) and OD stretching vibration (dotted line).

In the calculation of the nuclear dynamics, we set the reduced mass to be equal to 1 amu, since the mass of the escaping hydrogen atom is much smaller than the mass of the rest of the molecule. For the investigation of the isotope effect, i.e. in calculations of the D loss, the reduced mass was multiplied by two.

4. Results and discussion

4.1. (M–H)$^-$ ion yields

In figure 3, we present the yields for the (M–H)$^-$ ions for the three compounds and compare them with the theoretical results. Experimental and theoretical curves are normalized to each other at the peak, and the theoretical cross sections are convoluted with a Gaussian beam profile with the FWHM width of 0.1 eV.

All three ion yields show pronounced step-like structures at vibrational threshold. As is well known [34], threshold resonances and structures appear due to the long-range electron–molecule interaction, usually due to a combination of dipolar and polarization potentials. If the interaction is strong enough, it can support a bound state and a vibrational Feshbach resonance which is due to electron capture into a vibrationally excited state of the molecule. If the long-range interaction is not strong enough to support a bound state, it can lead to a virtual state which manifests itself as a pronounced cusp at the vibrational excitation threshold. In the present case, as in the case of formic acid [23], the features at vibrational thresholds are identified as virtual-state cusps. In figure 3, the energies for exciting the $\nu = 3$, 4 and 5 quanta of the OH stretching mode are marked by vertical lines, a value of 0.437 eV was used for the fundamental O–H stretch vibration $v_{OH} = 0 \rightarrow 1$. The step-like structures at the vibrational excitation thresholds are reproduced well by the theory, although in all three experimental cross-section curves, we find additional weak but reproducible structures.
Figure 3. Comparison of experimental data with the theoretical calculation for $\alpha$-, $\beta$- and $\gamma$-aminobutanoic acid. Experimental and theoretical curves are normalized to each other at the peak, and the theoretical cross sections are convoluted with a Gaussian beam profile with a FWHM of 0.1 eV.

(see vertical dotted lines) in the energy range between the $\nu = 3$ and $\nu = 4$ vibrational excitations. These features can be interpreted as the vibrational combination modes $3\nu_{\text{OH}} + \nu_{\text{CO}}$ and $3\nu_{\text{OH}} + \nu_{\text{C}=\text{O}}$, as suggested in a recent study on vibrational excitation of glycine, alanine and propanoic acid [12].

We observe a significant change in the shape of the $(\text{M–H})^-$ yield with the position of the amino group (–NH$_2$) in the molecule. The first feature that peaks sharply at about 1.2 eV and was observed in formic acid [6] and many $\alpha$-amino acids [8–13] becomes less pronounced for
Figure 4. Comparison of the results for β-aminobutanoic acid between experiment and theory with the two different parameterization models for the $R$-matrix surface amplitude: exponential and linear.

the β- and γ-compounds, which leads to novel cross-section shapes. This tendency has also been observed in a recent study on β-alanine [14]. We note that the appearance energy for the different (M–H)$^-$ ions is subjected to a small (about 40 meV) but clearly reproducible shift to higher energy on going along the line α-, β- and γ-aminobutanoic acid, showing the same trend as the calculated thresholds reported in table 1. When comparing both quantities it should be noted that the electron beam has an energy resolution of about 0.1 eV, while the accuracy of the calculation is about 0.15 eV. The difference in DEA cross sections along the line α-, β- and γ- is in part due to these different reaction thresholds. As the threshold increases, the crossing point between the neutral and anion curves is moved upward, resulting in less pronounced structures for the lowest overtone $\nu = 3$. In the case of the gamma compound (the bottom panel in figure 3), we can see that the calculated value for the threshold (1.33 eV) might be overestimated, as it cuts it off completely while the experimental data show a small but present contribution of this mode.

Moreover, when comparing experimental and theoretical curves in figure 3 one should remember that our theoretical model employs the same $R$-matrix parameters for all compounds; the only difference between compounds in our theoretical treatment is in the choice of different threshold energies and different dipole moments (table 1). However, in reality the difference in the short-range part of the electron–molecule interaction could be important too. To demonstrate this, we present the results of two sets of calculations for β-aminobutanoic acid in figure 4: one produced with the exponential model and the other with the linear model, as described in section 3. This figure demonstrates that, as in the case of formic acid [23], a small variation of the $R$-matrix parameters can significantly improve the agreement with the experiment.

4.2. Effect of deuteration on the dissociative electron attachment process

To further investigate the capability of our simple 1D $\sigma^*$ model to reproduce experimental observations, we studied the D loss from deuterated α-aminobutanoic acid ($\alphaAx{D}$). Experimental and theoretical cross sections are compared in figures 5(a) and (b), respectively, and again
present a similar overall trend. (i) The onset for \((\alpha A_D - D)^-\) is shifted to higher energies; the DEA threshold for the deuterated compound is indeed higher by about 0.1465 of the vibrational quantum for the nondeuterated compound (see figure 2). (ii) The cusps at vibrational threshold are less pronounced, the O–D stretch vibrational levels are denser and therefore convolution with the experimental energy profile tends to soften the features. (iii) The magnitude of the cross section for the deuterated compound is much lower (by a factor of 50, according to theory). This isotope effect, also observed in uracil and thymine [29, 35], is a direct consequence of a DEA reaction proceeding along a repulsive surface and subjected to strong autodetachment. Upon deuteration the time for dissociation of the transient anion increases, thereby decreasing the fragment anion formation in favor of autodetachment. Although the overall agreement between theory and experiment is reasonably good, we do observe some discrepancies; in particular, the calculation predicts a substantially narrower peak than observed experimentally. This actually reflects the same tendency that can be seen for nondeuterated compounds and might be due to the choice of \(R\)-matrix parameters as discussed above in the case of \(\beta\)-aminobutanoic acid.

We also calculated the DEA cross section for deuterium loss from the deuterated \(\beta\)- and \(\gamma\)-compounds that were not investigated experimentally. The results are presented in figure 6, where they are compared with all other calculated nonconvoluted cross sections for the investigated nondeuterated and deuterated compounds. The features at vibrational threshold are very prominent without convolution and as pronounced in deuterated compounds as in nondeuterated.

**Figure 5.** Comparison between \(\alpha\) (black) and deuterated \(\alpha\)-aminobutanoic acid (green) for (a) experiment and (b) theory.
4.3. Temperature effect

Since the DEA cross section grows strongly with \( \nu_{in} \), the initial vibrational quantum number of the molecule, a pronounced temperature effect can be observed for many molecules. However, because of the large vibrational quantum for the O–H stretch in the present compounds, we cannot expect the temperature effect to be particularly strong, but rather similar to that for hydrogen halides [36] and uracil [29]. Our calculations show that the DEA cross sections at \( T = 400 \) K are practically indistinguishable from those at \( T = 0 \) K. Only for higher temperatures does the effect become noticeable. In figure 7, we present calculated DEA cross sections for the \( \alpha \) compound (deuterated and nondeuterated) at \( T = 700 \) K. The cross section becomes nonzero below the thermodynamic threshold, which is particularly noticeable for the deuterated compound.

5. Conclusion

The present study shows that DEA via \( \sigma^* \)-resonance is a fundamental mechanism in the dissociation of carboxyl group-containing molecules at electron energies close to 1 eV. We have observed pronounced features in DEA cross sections for \( \alpha-, \beta- \) and \( \gamma- \)aminobutanoic acids similar to those observed and calculated for hydrogen halides and formic acid: threshold onsets and cusps at vibrational excitation thresholds. These features can be described by theory utilizing a \( \sigma^* \)-resonance model incorporating long-range (dipolar and polarization) interaction.
Figure 7. Nonconvoluted and convoluted cross sections at $T = 700 \, \text{K}$ for both $\alpha$- and deuterated $\alpha$-aminobutanoic acids.

between the incoming electron and the target molecule. The $R$-matrix approach employing the previously developed model for formic acid allows us to explain the main features of the DEA cross sections for nondeuterated and deuterated compounds and, moreover, predicts the magnitude of the isotope effect and the temperature effect.

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References

[1] Aflatooni K, Gallup G A and Burrow P D 1998 J. Phys. Chem. A 102 6205–7
[2] Hanel G, Gstir B, Denifl S, Scheier P, Probst M, Farizon B, Farizon M, Illenberger E and Märk T D 2003 Phys. Rev. Lett. 90 188104
[3] Abdoul-Carine H, Gohlke S and Illenberger E 2004 Phys. Rev. Lett. 92 168103
[4] Ptasinska S, Denifl S, Scheier P, Illenberger E and Märk T D 2005 Angew. Chem., Int. Ed. Engl. 44 6941–3
[5] Scheer A M, Aflatooni K, Gallup G A and Burrow P D 2005 Phys. Rev. Lett. 92 068102
[6] Pelc A, Sailer W, Scheier P, Probst M, Mason N J, Illenberger E and Märk T D 2002 Chem. Phys. Lett. 361 277–84
[7] Martin I, Skalicky T, Langer J, Abdoul-Carine H, Karwasz G, Illenberger E, Stano M and Matejčík S 2005 Phys. Chem. Chem. Phys. 7 2212–6
[8] Gohlke S, Rosa A, Illenberger E, Brüning F and Huels M A 2002 J. Chem. Phys. 116 10164–9
[9] Ptasinska S, Denifl S, Candori P, Matejčík S, Scheier P and Märk T 2005 Chem. Phys. Lett. 403 107–12
[10] Papp P, Urban J, Matejčík S, Stano M and Ingolfsson O 2006 J. Chem. Phys. 125 204301

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[11] Vasil’ev Y V, Figard B J, Barofsky D F and Deinzer M L 2007 Int. J. Mass Spectrom. 268 106–21
[12] Abouaf R 2008 Chem. Phys. Lett. 451 25–30
[13] Kocisek J, Papp P, Mach P, Vasil’ev Y V, Deinzer M L and Matejcik S 2010 J. Phys. Chem. A 114 1677–83
[14] Vizcaíno V, Bartl P, Gschliesser D, Huber S E, Probst M, Märkl T D, Scheier P and Denifl S 2011 Chem. Phys. Chem. 12 1272–9
[15] von Sonntag C 1987 Chemical Basis for Radiation Biology (London: Taylor and Francis)
[16] von Sonntag C 2006 Free Radical Induced DNA Damage (Berlin: Springer)
[17] Cobut V, Fongillo Y, Patau J P, Goulet T, Fraser M J and Jay-Gerin J P 1998 Radiat. Phys. Chem. 51 229
[18] Boudaïffa B, Cloutier P, Hunting D, Huels M A and Sanche L 2000 Science 287 1658–60
[19] Martin F, Burrow P D, Cai Z, Cloutier P, Hunting D and Sanche L 2004 Phys. Rev. Lett. 93 068101
[20] Sanche L 2005 Eur. Phys. J. D 35 367
[21] Chase J W and Williams K R 1986 Annu. Rev. Biochem. 55 103–36
[22] Rescigno T N, Trevisan C S and Orel A E 2006 Phys. Rev. Lett. 96 213201
[23] Gallup G A, Burrow P D and Fabrikant I I 2009 Phys. Rev. A 79 042701
[24] Kubala D, May O and Allan M 2012 XXVII ICPEAC (Belfast, 2011) J. Phys. Conf. Series at press
[25] Denifl G, Muigg D, Stamatovic A and Märkl T D 1998 Chem. Phys. Lett. 288 105–10
[26] Horáček J and Domcke W 1996 Phys. Rev. A 53 2262–71
[27] Domcke W 1991 Phys. Rep. 208 97–188
[28] Fabrikant I I 1991 Phys. Rev. A 43 3478–86
[29] Gallup G A and Fabrikant I I 2011 Phys. Rev. A 83 012706
[30] Nemukhin A V, Grigorenko B L and Granovsky A A 2004 Mosc. Univ. Chem. Bull. 45 75
[31] Schmidt M W et al 1993 J. Comput. Chem. 14 1347–63
[32] Curtiss L A, Redfern P C and Raghavachari K 2004 J. Chem. Phys. 120 124105
[33] Frisch M J et al 2009 Gaussian 09 Revision A.1 (Wallingford, CT: Gaussian)
[34] Hotop H, Ruf M W, Allan M and Fabrikant I 2003 Adv. At. Mol. Opt. Phys. 49 85–216
[35] Denifl S, Sulzer P, Zappa F, Moser S, Kräutler B, Echt O, Bohme D, Märkl T D and Scheier P 2008 Int. J. Mass Spectrom. 277 296–9
[36] Čížek M, Horáček J and Domcke W 1999 Phys. Rev. A 60 2873–81

New Journal of Physics 14 (2012) 043017 (http://www.njp.org/)