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Supporting Information Production of doubly-charged highly reactive species from the long-chain amino acid GABA initiated by Ar⁹⁺ ionization

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Double electron capture.

Detailed statistics of ab initio molecular simulations (AIMD) related with Coulomb explosion (CE) of $GABA^{2+}$ molecules are shown in Fig. 1a). The fragmentation yield of CE processes: (1), (2), (3), and (4) is presented as a function of excitation energy. In Fig. 1b) we also present the optimised fragments taken from MD simulations with their relative energy (in parenthesis); mechanisms are associated according to the classification of the bond cleavage. We can also see that the probability of the CE processes (3) and (4) is much higher than for other CE types. $C_{carboxyl} - C_{\alpha}$ bond cleavage (1) starts to increase with the excitation energy but even for 4 eV of excitation energy it is still significantly less probable than other CE mechanisms. Interestingly, in Fig. 1b) we observe 3 and 4-member ring structures after $C_{carboxyl} - C_{\alpha}$ and $C_{\beta} - C_{\gamma}$ bond cleavages (channels (1) and (3), respectively). Considering three body fragmentation of $GABA^{2+}$ (process (4) in Fig. 1) charge could be hypothetically distributed in six different ways: a) $NH_2CH_2^+ + CH_2CH_2 + COOH^+$, b) $\mathrm{NH_2CH_2^+} + \mathrm{CH_2CH_2^+} + \mathrm{COOH, \ c) \ \mathrm{NH_2CH_2}} + \mathrm{CH_2CH_2^+} + \mathrm{COOH^+, \ d) \ \mathrm{NH_2CH_2^{2+}}} + \mathrm{CH_2CH_2} + \mathrm{COOH, \ c) \ \mathrm{NH_2CH_2^{2+}}} + \mathrm{CH_2CH_2^{2+}} +$ e) $NH_2CH_2 + CH_2CH_2^{2+} + COOH \text{ or } f$) $NH_2CH_2 + CH_2CH_2 + COOH^{2+}$. The MD simulations reveal that among them, only a) and b) are noticed with 92.7% and 7.3% probabilities, respectively. Total contribution of the channels 4a and 4b to the MD statistics for double electron capture is 32.4%and 2.5%, respectively. Moreover, the former exit channel (4a) is 2 eV lower in energy. We also



Figure 1: Ab initio molecular dynamics statistics for all 30 dications of GABA. Competition between different Coulomb bond cleavages. The number in parentheses represents different bonds breaking: (1) $C_{carboxyl} - C_{\alpha}$, (2) $C_{\alpha} - C_{\beta}$, (3) $C_{\beta} - C_{\gamma}$ and (4) $C_{carboxyl} - C_{\alpha} + C_{\beta} - C_{\gamma}$ bond cleavages; a) fragmentation yield as a function of the excitation energy (in eV); b) optimised MD exit channels with DFT-B3LYP/6-311G(d,p) level of theory, where the numbers in brackets indicate the relative energy in respect with the most stable fragmentation channel in eV.

see that $C_{\beta} - C_{\gamma}$ (3) dominates over another 2 body fragmentation in the whole range of excitation energies. One would expect that in the longer simulation timescale the (3) process will contribute to the (4) due to the further $C_{carboxylic} - C_{\alpha}$ bond breaking of the CH_2COOH^+ ending up either on $CH_2CH_2 + COOH^+$ (2.20 eV) or $CH_2CH_2^+ + COOH$ (4.23 eV).

Two intense coincidence islands $26^+/28^+$ and $27^+/28^+$ related with CE processes are analysed in details on the potential energy surface (PES) (see Fig. 2) in order to gain a better understanding of the experimental measurements. We observe, not only similar relative energies (6.77 and 7.08 eV) but also similar energy barriers. It explain similar experimental relative intensities measured in the experiment (3.2% and 2.5%). Even if the relative theoretical and experimental comparison between both channels are in an agreement we see that both channels are much higher in the energy than the ones presented in the Tab. 1 in main article and involve high energy barriers on PES. However, both pathways can be derived from MD simulations (3) and (4) after neutral H and H₂ emissions as a kinetically favorable processes. This emphasises the role of the molecular dynamics simulations to properly describe fragmentation.



Figure 2: Fragmentation pathways for doubly positively charged GABA. Only the stationary points of the potential energy surface corresponding to $C_{\beta} - C_{\gamma}$ bond breaking and further hydrogen emission leading to charged fragments: m/z=28 amu with other heavy fragments (m/z=26 and 27 amu). Relative energies, ΔE , are given in eV at the DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction with respect to the exit channel: NH₂CH₂⁺ + CH₂CH₂ + COOH⁺, which is exothermic with respect to GABA²⁺ by 5.28 eV (see Tab. 1 in main article).



Figure 3: Statistics of the AIMD simulations showing isomerisation competition for $GABA^{2+}$. The number in parentheses represents different geometry reorganisation of dication of GABA taken from the MD simulation and than optimised at the DFT-B3LYP/6-311++G(d,p) level of theory.



Figure 4: AIMD simulations showing combined processes competition for $GABA^{2+}$.

The degeneracy of another exit channels: $NHCH^+ + H_2 + CH_2CH_2 + COOH^+$ and $NH_2CH_2^+ + CH_2CH_2^+ + COOH$ explains the similar experimental (relative intensity) and theoretical (relative energy) values (see Tab. 1 in main article).

In the Fig. 3 we see results of MD simulation for $GABA^{2+}$, without bond breaking; H-migration leads to stable isomers (denoted as (5a-f)). The highest yield is observed for diol ²⁺ isomers.

Fig. 4 shows combined processes for $GABA^{2+}$ which are related with the emission of neutrals before or after CE and isomerisation. The probability of occurrence of the combined processes increases with the excitation energy (see Fig. 4). It is not surprising, as the additional excitation energy given to the vibrational degrees of freedom can induce many secondary reactions.

Possible structures corresponding to doubly charged fragments (m/z = 26.5, 27.5, 28.5 amu) of reactive nitrogen species (RNS) observed in experiment and extensively discussed in main article are presented Fig. 5. The structure of cyclic bigger doubly charged moieties are shown in Fig. 6. Reactive oxygen species (ROS) with the same masses as RNS described above, proposed to be formed in the fragmentation of GABA³⁺ are presented in Fig. 10. Some of those structures are obtained after the optimisation of neutral molecules taken from the NIST database,¹ the rest is obtained after optimisation of the fragments observed in the MD. According to previous study of the absorption and fluorescence spectra of microporous polymers,² even if the ring structures are not in their lowest energy conformation we can expect them to play an important role.



Figure 5: Possible structures of doubly charged cations at m/z = 26.5, 27.5 and 28.5 amu optimised at the DFT-B3LYP/6-311++G(d,p) level of theory. Relative energies in parentheses between the conformers are in eV. Fragments with star (*) were optimised of the corresponding neutral structure taken from National Institute of Standards and Technology (NIST).



Figure 6: Possible structures of doubly charged cations at m/z = 39.5, 40.5 and 41.5 amu optimised at the DFT-B3LYP/6-311++G(d,p) level of theory. Relative energies in parentheses between the conformers are in eV. Fragments with star (*) were optimised of the corresponding neutral structure taken from NIST.



Figure 7: Ab initio molecular dynamics statistics for all 30 trications of GABA. Competition between different Coulomb bond cleavages; fragmentation yield as a function of the excitation energy (in eV). The number in parentheses represents different bonds breaking: (1) $C_{carboxyl} - C_{\alpha}$, (2) $C_{\alpha} - C_{\beta}$, (3) $C_{\beta} - C_{\gamma}$ and (4) $C_{carboxyl} - C_{\alpha} + C_{\beta} - C_{\gamma}$ bond cleavages.

Triple electron capture

Total contribution of direct bond breaking for GABA³⁺ related with CE is presented in Fig. 7. The CE processes are very similar in the full excitation energy range to GABA²⁺ fragmentation discussed previously, (see Fig.7) considering that the $C_{\beta} - C_{\gamma}$ become the dominant pathway for three electron capture phenomena and in the slightly longer simulation time scale will break in three fragments similar to GABA²⁺.

MD simulation for GABA³⁺ without bond breaking are presented in Fig. 8. H-migration leads to isomers denoted as (5a-e). The highest yield is observed for $[NH_3 - R]^{3+}$ forms, where R is the rest of the molecule without one hydrogen.

Fig. 9 shows combined processes for GABA³⁺. The fragmentation yield of the combined processes increases with the excitation energy similarly to GABA²⁺. The most important processes classified as combined for GABA³⁺ fragmentation correspond to emission of H₂ molecules (6e and 6f) with subsequent $C_{carboxylic} - C_{\alpha}$ bond cleavage i.e. COOH⁺ emission (6b) and (6y) NH₂CCH⁺₃ + CH⁺₃ + COOH⁺.



Figure 8: Statistics of the AIMD simulations showing isomerisation competition for $GABA^{3+}$.



Figure 9: AIMD simulations showing combined processes competition for $GABA^{3+}$.



Figure 10: Possible structures of doubly charged cations at m/z = 26.5, 27.5 and 28.5 amu optimised at the DFT-B3LYP/6-311++G(d,p) level of theory related to ROS - containing oxygen. Relative energies in parentheses between the conformers are in eV. Fragments with star (*) were optimised of the corresponding neutral structure taken from National Institute of Standards and Technology (NIST).

The possible optimised reactive oxygen species (ROS) are presented in Fig. 10. These doubly charged moieties are produced only in the fragmentation of $GABA^{3+}$ due to different double charge localisation in comparison with $GABA^{2+}$.

Fig. 11 presents the analysis of the charges on the emitted hydrogen molecules related with combined processes. The Mulliken charges for H_2 , as it is shown in the panel a) oscillates as a number of counts (bin of 0.01). Panel b) present the counts for H_2 charges considering the threshold smaller than the value of the charge (0 to 1 with 0.01 bin). The plots shows that the charge state of hydrogen molecules vary depending on the criteria. There is no clear neutral (q=0) or charged

			$C_{carboxvlic} - C_{\alpha} +$		
$C_{\text{carboxylic}} - C_{\alpha}$ (1)	$C_{\alpha} - C_{\beta}$ (2)	$\mathrm{C}_eta - \mathrm{C}_\gamma \ (3)$	$C_{\beta} - C_{\gamma}$ (4)	Isomerisation (5)	Neutral emission (6)
			NH CH ⁺		NH ₂ CH ⁺
NH ₂ CHCH ₂ CH ⁺	NH ₂ CHCH ⁺	$NH_{0}CH^{+}$	$\Gamma_2 C \Gamma_2$		$\square_2 \square_2$
	$\perp CH_2COOH^+$	$\pm CH_{2}CHCOOH^{+}$	+C12C112 $+COOH^{\pm}$	NH ₂ CHCH ₂ CH ₂ COOH ²⁺	$+C\Omega_2$
(1a)	(2a)	(3a)	+00011* (4a)	(5a)	(6a)
(14)	(24)	(64)	NH CH ⁺	(00)	(04)
	NH CHCH+	NH CH ⁺	$N_{12}O_{12}$		NUL OU OUOU $^{2+}$
$h_2 C h_2 C h_2 C h_2$	\downarrow CIL COOLI+	\downarrow CIL CIL COOU+	$+CH_2CH_2$	NH ₂ CHCH ₂ CH ₂ C(OH) ²⁺	$h_3 CH_2 CH CH_3$
+COOH'	$+CH_2COOH$	$+CH_2CH_2COOH'$	+COOH	(5b)	$+CO_2$
(10)	(20)		(40)	(30)	(00)
$\rm NH_2CHCH_2CH_3^+$	$NH_2CHCH_2^+$	NH ₂ CH ₂			$\rm NH_3CH_2CH_2CH_2^{2+}$
$+COOH^+$	$+CH_3COOH^+$	$+CH_2(CH_2O)COH^+$		$NH_3CHCHCH_2C(OH)_2^{2+}$	$+CO_2$
(1c)	(2c)	(3c)		(5c)	(6c)
					$\rm NH_2CH_2^+$
$\rm NH_2(CH_2CH)CH_3^+$		$NH_2CH_2^+$			$+CH_3CHOH^+$
$+COOH^+$		$+CH_2(CH_2CO)OH^+$		$\rm NH_2CHOCOHCH_2CH_3^{2+}$	+CO
(1d)		(3d)		(5d)	(6d)
		NIL CIL+			$\rm NH_2CHCH_3^+$
$\rm NH_3CH_2CHCH_2^+$		NH ₂ CH ₂			$+CH_2OH^+$
$+COOH^+$		$+CH_2CHC(OH)_2^+$		$CH_2CH(NH_3)CH_2COOH^{2+}$	+CO
(1e)		(3e)		(5e)	(6e)
$NH_3CH(CH_2)_2^+$		$NH_2CH_2^+$			NH ₃ CHCHCH ₂ COOH ²⁺
$+COOH^+$		$+HOCH_2CH_2CO^+$		NH ₂ CHCH ₂ OCCH ₂ OH ²⁺	$+H_2$
(1f)		(3f)		(5f)	(6f)
					$\rm NH_2CCHCH_2C(OH)_2^{2+}$
					$+H_2$
					(6g)
					NHCCH ₂ CH ₂ C(OH) ₂ ²⁺
					$+H_2$
					(6h)
					$NH_2COCOH(CH_2)^{2+}_{2+}$
					+H ₂
					(6i)
					NH ₂ CHCH ₂ CHCOOH ²⁺
					+H ₂
					(6j)
					NH ₂ CCH ₂ COHOCH ₂ ²⁺
					+H ₂
					(6k)
<u> </u>					NH ₂ CHCHCH ⁺
					$+H_{2} + COOH^{+}$
					(61)
					NH ₂ CHCH ₂ CH ₂ CO ²⁺
					$+H_2O$ (6m)
					NH ₃
					$+CH_2CHOCOHCH_2^{2+}$
					(6n)
					(***)

Table 1: All 37 mechanisms for the fragmentation of $GABA^{2+}$ molecules.

C C	C C	C C	$C_{carboxylic} - C_{\alpha} + C_{\alpha}$		NT (1 · · · 1 1 · 1
$C_{\text{carboxylic}} = C_{\alpha}$ (1)	$C_{\alpha} = C_{\beta}$ (2)	$C_{\beta} = C_{\gamma}$ (3)	$C_{\beta} = C_{\gamma}$ (4)	Isomerisation (5)	Neutral emission and combined processes (6)
(1)	(2)	(0)	NH ₂ CH ⁺	(8)	(0) NH ₂ C(CH ₂) ²⁺
$\rm NH_2CH_2CHCH_3^{2+}$	$\rm NH_2CHCH_2^{2+}$	$\rm NH_2CH_2^+$	$+CH_2CH_2^+$		$+H_2$
$+COOH^+$	$+CH_3COOH^+$	$+CH_2CH_2COOH^{2+}$	$+COOH^+$	$\rm NH_2CH_2CH_2COOH^{3+}$	$+COOH^+$
(1a)	(2a)	(3a)	(4a)	(5a)	(6a)
NH ₂ CH ₂ CH ₂ CH ₂ ²⁺	NH ₂ CHCH ²⁺	$NH_{2}CH_{2}^{+}$			NH ₂ CHCHCH ₂
$+COOH^+$	$+CH_2COOH^+$	$+CH_3CHCOOH^{2+}$		NH ₂ CHCH ₃ CH ₂ COOH ³⁺	$+COOH^+$
(1b)	(2b)	(3b)		(5b)	(6b)
NIL OHOL OH2+	NIL CHCH2+	NIL CII ⁺			$NH_2CCH_2CH_2^{2+}$
NH ₂ CHCH ₂ CH ₃	$\Gamma_{1}^{\text{NH}_{3}\text{CHCH}_{2}}$	$\Gamma \Pi_2 C \Pi_2$		NH-CHCH-CH-COOH ³⁺	$+H_2$
(1c)	(2c)	+CH2OCCH2OH (3c)		(5c)	+COOH (6c)
		()			NH ₂ CCHCH ₃ ²⁺
$\rm NH_3CH_2CHCH_2^{2+}$	$\rm NH_2CH_2CH_2^{2+}$	$NH_2CH_2^+$			$+\mathrm{H}_2^+$
$+COOH^+$	$+CH_2COOH^+$	$+CH_2(CH_2CO)OH^{2+}$		NH ₃ CH ₂ CHCH ₂ COOH ³⁺	+COOH
(1d)	(2d)	(3d)		(5d)	(6d)
NH ₃ CHCHCH ² ₃ ⁺				NU CHOU CH COH O3+	NH ₂ CCH ₂ CH ₂ COOH ³⁺
+COOH (1e)				(5e)	+H2 (6e)
$NH_3CH(CH_2)_2^{2+}$				(00)	NH ₂ CHCHCH ₂ COOH ³⁺
+COOH ⁺					$+H_2$
(1f)					(6f)
					NH ₂ CHCH ₂ CHCOOH ³⁺
					+112 (6g)
					CH ₂ COHOCNH ₂ CH ₂ ³⁺
				Neutral emission and combined processes cont.	$+H_2$
				(6)	(6h)
				NHCCH ₂ CH ₂ COOH ²⁺	$NH_2CCHCH_2C(OH)_2^{3+}$
				$+11_3$ (6r)	$+H_2$ (6i)
				NH ₂ CHCHCH ₂ ²⁺	NHCCH-CH-C(OH) ³⁺
				$+C(OH)_{2}^{+}$	$+H_2$
				(6s)	(6j)
				$NH_2CCHCH_2^+ + COOH^+$	NH ₂ CCHCH ₂ C(OH) ³⁺ ₂
				$+\mathrm{H_3^+}$	$+H_{2}$
				(6t)	(6k)
				$NH_{2}CH_{2}CHCH^{2+} + CO^{+}$	$NH_2CCH_2^{2+} + CH_2COOH^+$
				(6n)	$+ n_2$ (61)
				NH ₂ CHCH ₂ CH ₂ CO ²⁺	$NH_2CH^+ + CH_2CH_2^+$
				$+\mathrm{H_2O^+}$	+COOH ⁺
				(6v)	(6m)
				$\rm NH_2 CCHCH_2 CO^{2+}$	$NH_2CHCH_2^{2+}$
				$+H_2O^+ + H_2$	$+ OCCH_3^+ + OH$
					(6n)
				$NH_2UHUH_2UH_2^+ + H^+$	$N\Pi_2 \cup \Pi \cup \Pi_2$
	1	1	1	+UUUH'	+0.12001120 + 0.1120
				(6x)	(60)
				$\frac{(6x)}{\text{NH}_2\text{CCH}_3^+ + \text{CH}_3^+}$	(60) NH ₂ CH ⁺ ₂
				$(6x)$ $NH_2CCH_3^+ + CH_3^+$ $+COOH^+$	$(6o) \\ NH_2CH_2^+ \\ +CH_2COH^+ + CH_2O$

Table 2: All 44 mechanisms for the fragmentation of $GABA^{3+}$ molecules.



Figure 11: The counts of the 323 fragmentation mechanisms related with H_2 emission observed in combined processes. Panel a) shows the counts for different charges of the hydrogen molecules (q H_2); panel b) shows the normalised (to 100%) counts for q<threshold as a function of the threshold.

(q=1) H₂ molecule emission. We consider emission of charged hydrogen molecules if q>0.9, otherwise neutral evaporation is taking place (see Tab. 2). This criteria allow us to assign double charge to the nitrogen reactive species in coincidence with COOH⁺ (see 6a-d in Tab. 2).

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