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Supporting information for article:

Comprehensive model for X-ray-induced damage in protein crystallography

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(a) b) (c)

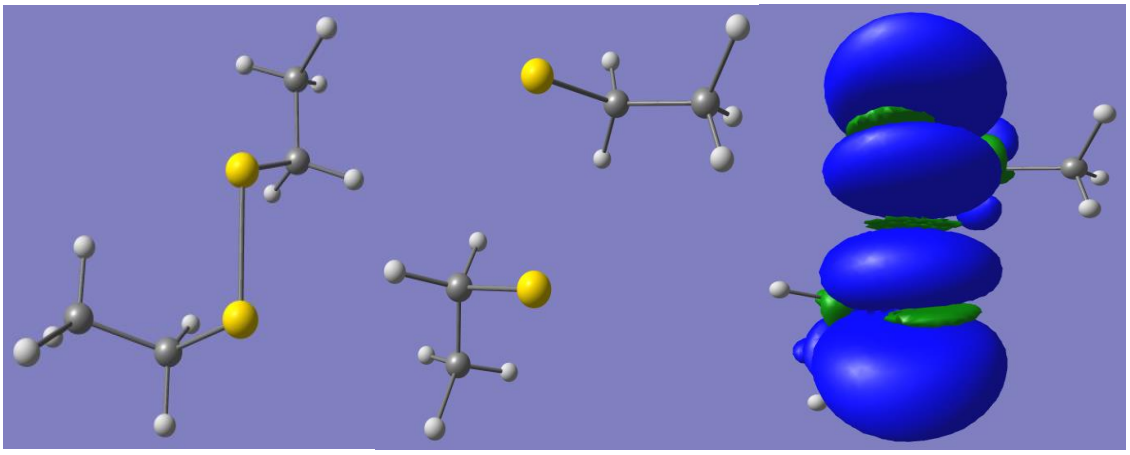

Figure S1 (a) Model used for cystine calculations (S-S bond 2.0839 Å), (b) Calculations on the cystine radical anion results in an extension of the S-S bond to 2.934 Å, (c) Spin density for the cystine radical anion $RSSR^{\bullet -}$ in vacuum or in dielectric medium (SMD, ε=2.5), both are valence bound anions.

(a) (b)

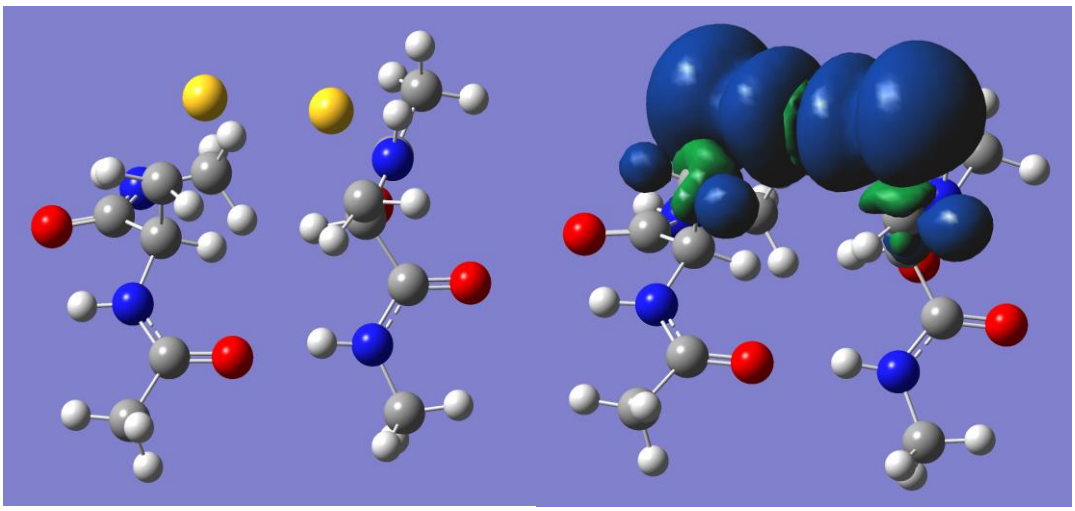

Figure S2 (a) Model used for cystine calculations (S-S bond 2.0839 Å), (b) Calculations on the cystine radical anion results in an extension of the S-S bond to 2.934 Å, (c) Spin density for the cystine radical anion $RSSR^{\bullet -}$ in vacuum or in dielectric medium (SMD), both are valence anions.

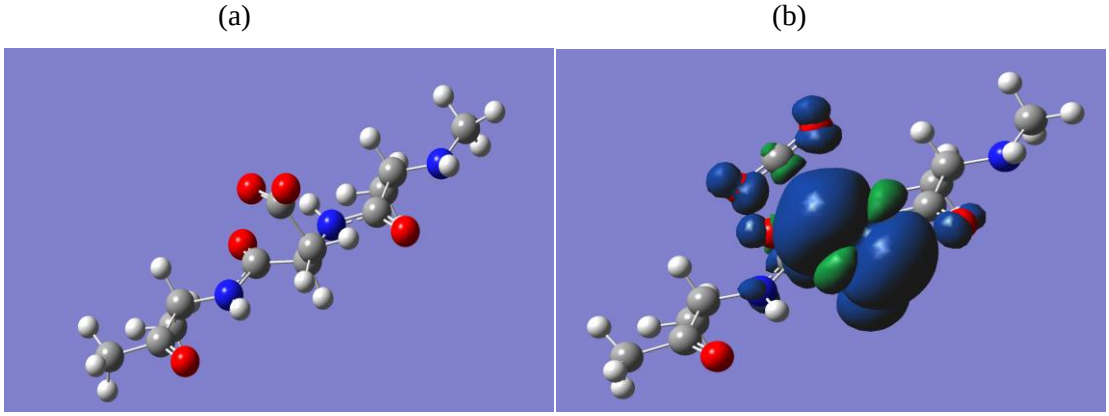

Figure S3 (a) The short tripeptide Ala-Asp-Ala. The optimization reached a stationary point with a CO_2 separation of 1.61Å. Clearly the CO_2 is not linear. (b) The CO_2 separation is now 3.0 Å. Now the CO_2 is linear and one sees that almost all of the spin density is on the $-CH_2^{\bullet}$,

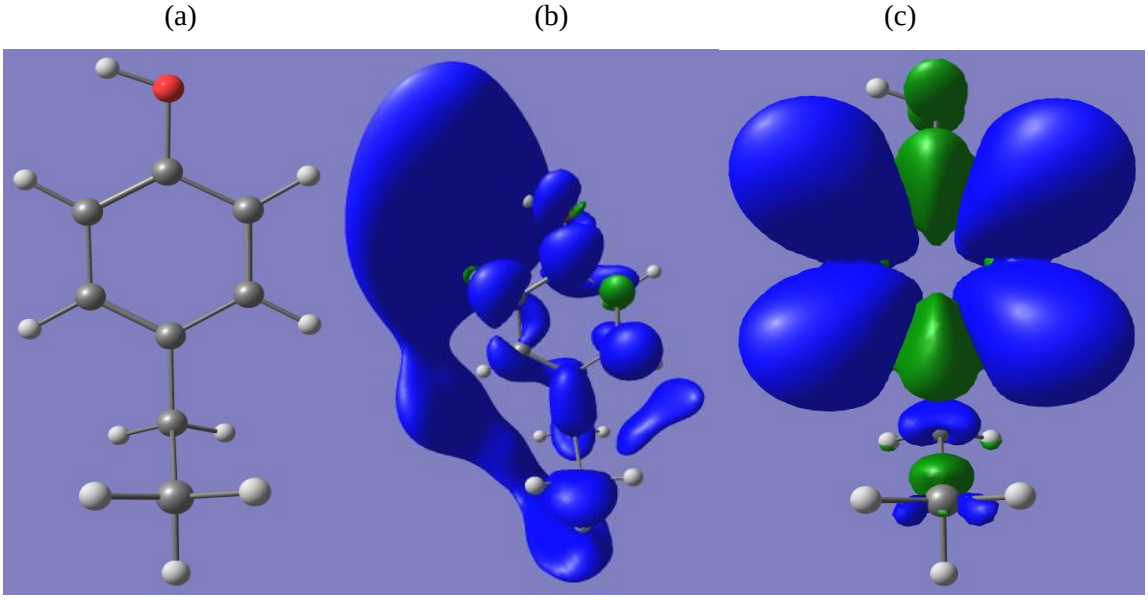

Figure S4 (a) Structure of model used for tyrosine sidechain, (b) Calculated dipole bound anion of tyrosine, and (c) Same model calculated with a dielectric medium (ε=2.5) yields the valence bound anion of tyrosine.

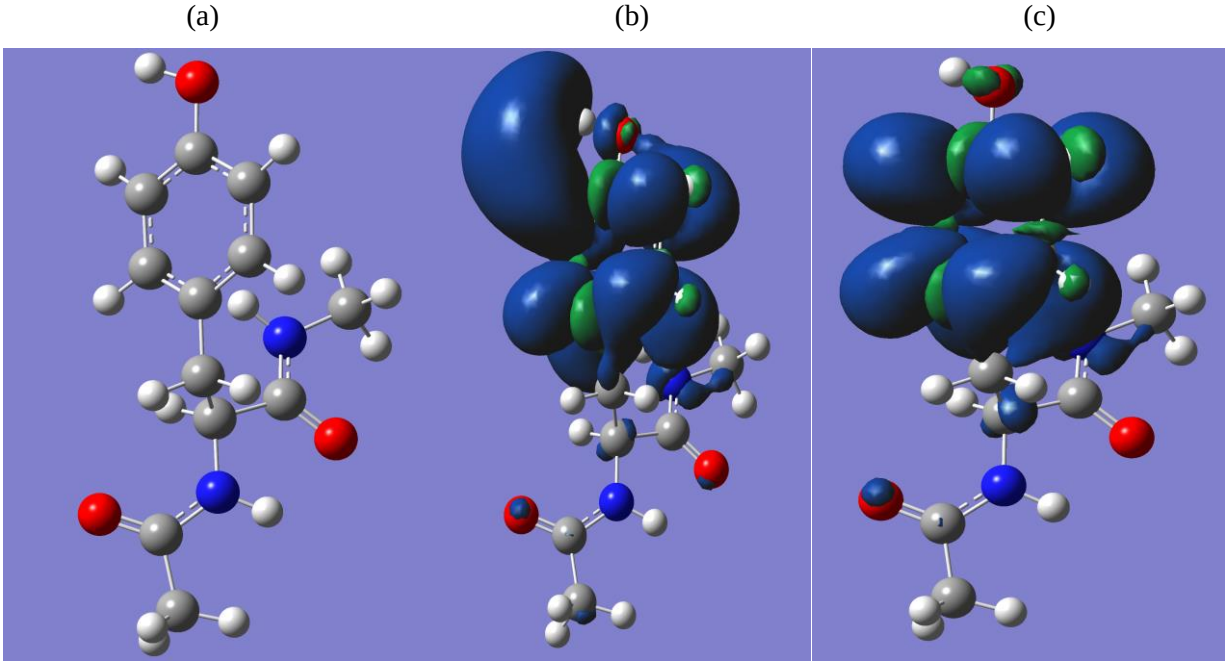

Figure S5 (a) Structure of short peptide model for tyrosine. Note that the tyrosine ring is tilted slightly so as not to cover up some of the peptide. (b) Calculated dipole bound anion of tyrosine, and (c) Same model calculated with a dielectric medium (ε=2.5) yields the valence bound anion of tyrosine.

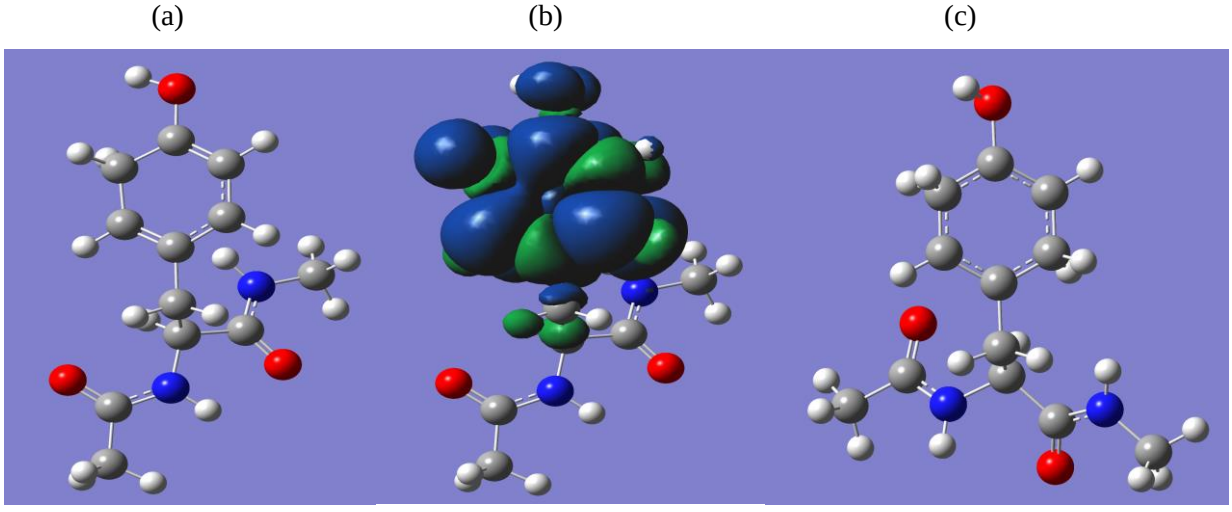

Figure S6 (a) The neutral radical Tyr(C+H)• (b) The spin density of the neutral radical Tyr(C+H)• is almost all on the tyrosine ring. (c) A figure of the final product after two one-electron reductions to yield dihydro-Tyrosine.

(a) (b) (c)

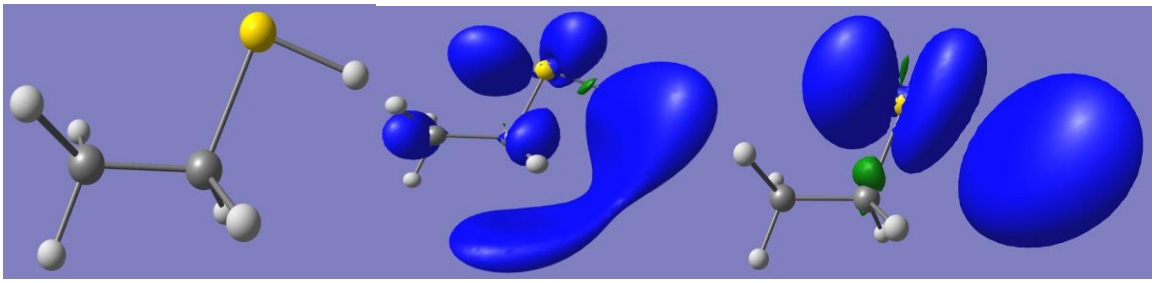

Figure S7 (a) Model of cysteine used in calculations, the S-H bond length is 1.415 Å, (b) Calculated DB Anion of cysteine, with the S-H bond length expands to 1.848 Å, and (c) Same model calculated with a dielectric medium (ε=2.5) yields the VB anion of cysteine.

(a) (b)

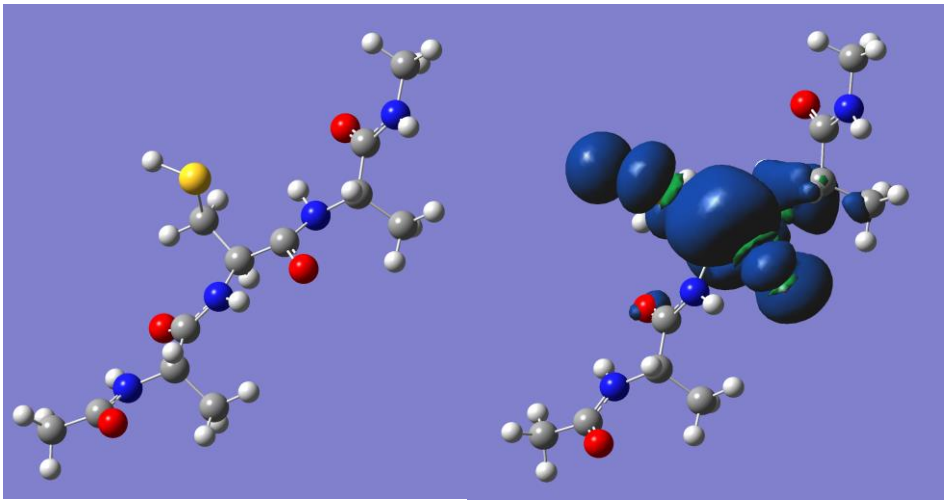

Figure S8 a) Structure of the protein model Ala-Cys-Ala, and b) Spin density of the cysteine anion radical.

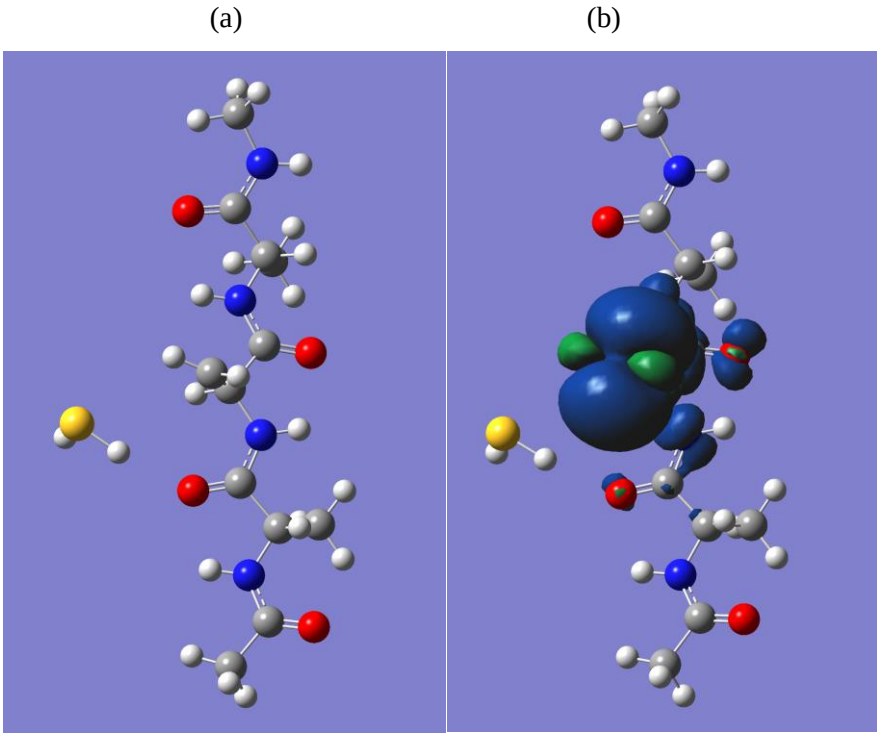

Figure S9 (a) An optimized structure of the protein model Ala-Cys-Ala cysteine anion radical is protonated to form a $–CH_2^{\bullet}$ radical on the peptide backbone. Here the SH_2 ---- $CH_2^{\bullet}$ separation is 3.91Å. Almost all of the spin density is on the $–CH_2^{\bullet}$ from the *ca.* 24 G methylene protons (Figure S12b).

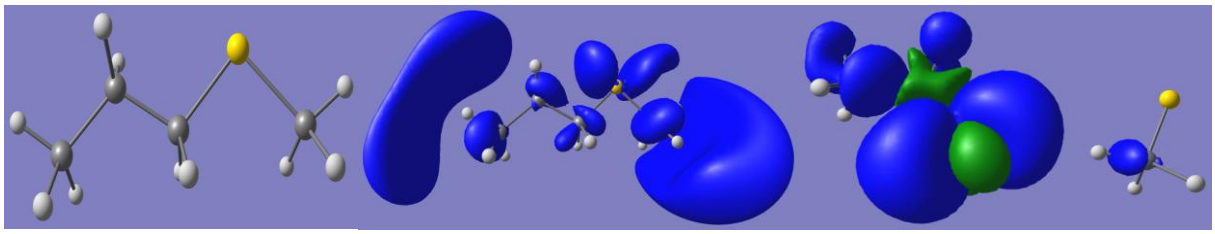

Figure S10 (a) Model of methionine used in calculations, the S-CH_3 bond length is 1.848 Å, (b) Calculated DB anion of cysteine, and (c) Same model calculated with a dielectric medium (ε=2.5) yields the VB anion of methionine with most of the spin density on -CH_3-CH_2. Here the S-CH_3 has dissociated.

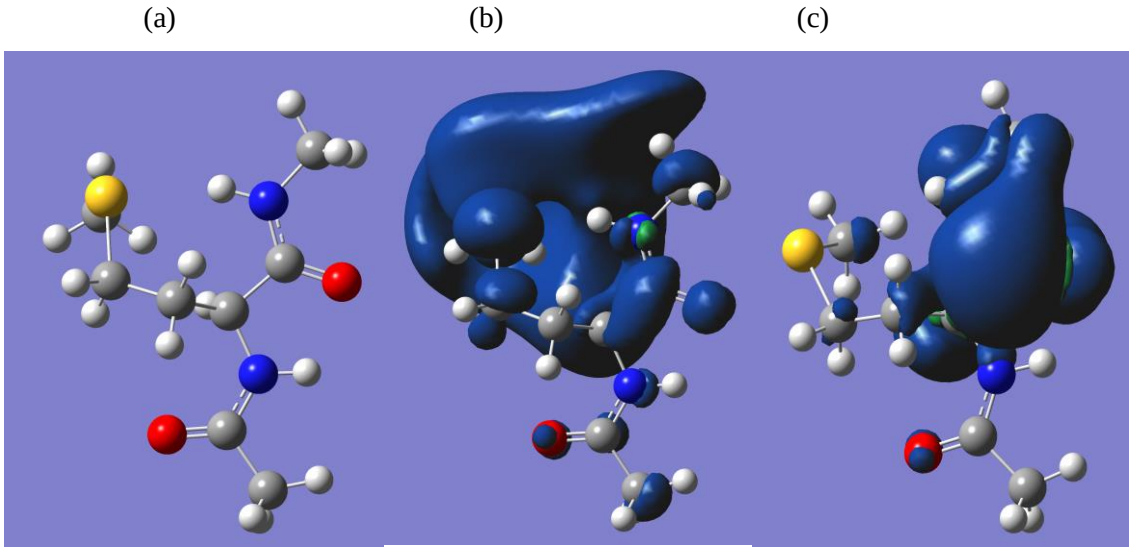

Figure S11. (a) The small peptide model with the methionine side chain. (b) shows the reduction pathway with a large dipole bound anion centered on the sulfur -CH_3. (c) shows that the dipole bound anion can be converted to a valence bound structure (using a dielectric constant of 2.5).

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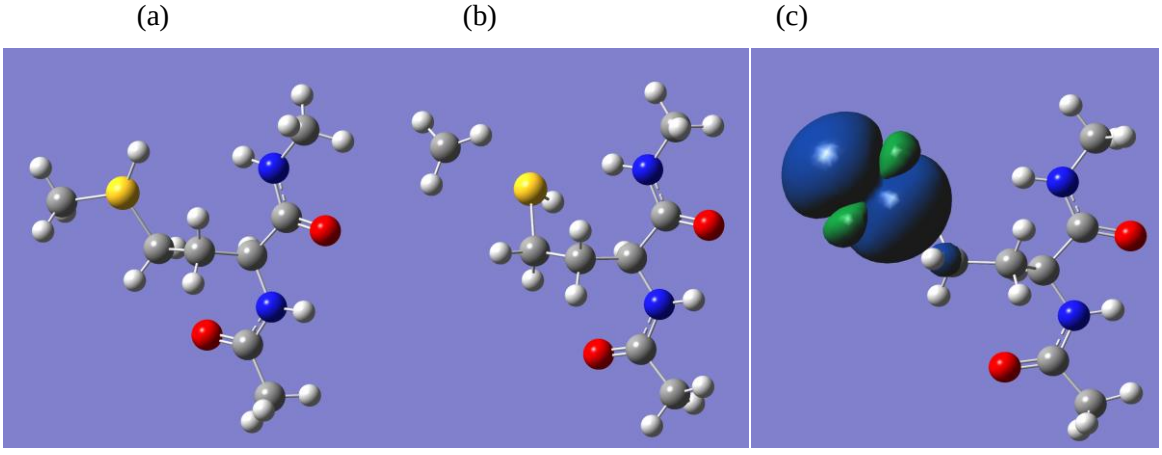

Figure S12 (a) The small peptide model for methionine with an additional proton on the sulfur. This structure is unstable and after just a few iterations the methyl group dissociates. (b) the S – CH_3 separation is 4.8 Å. (c) shows the spin density of this structure with all of the spin on the methyl group. Here the three hyperfine couplings are ~23 G.

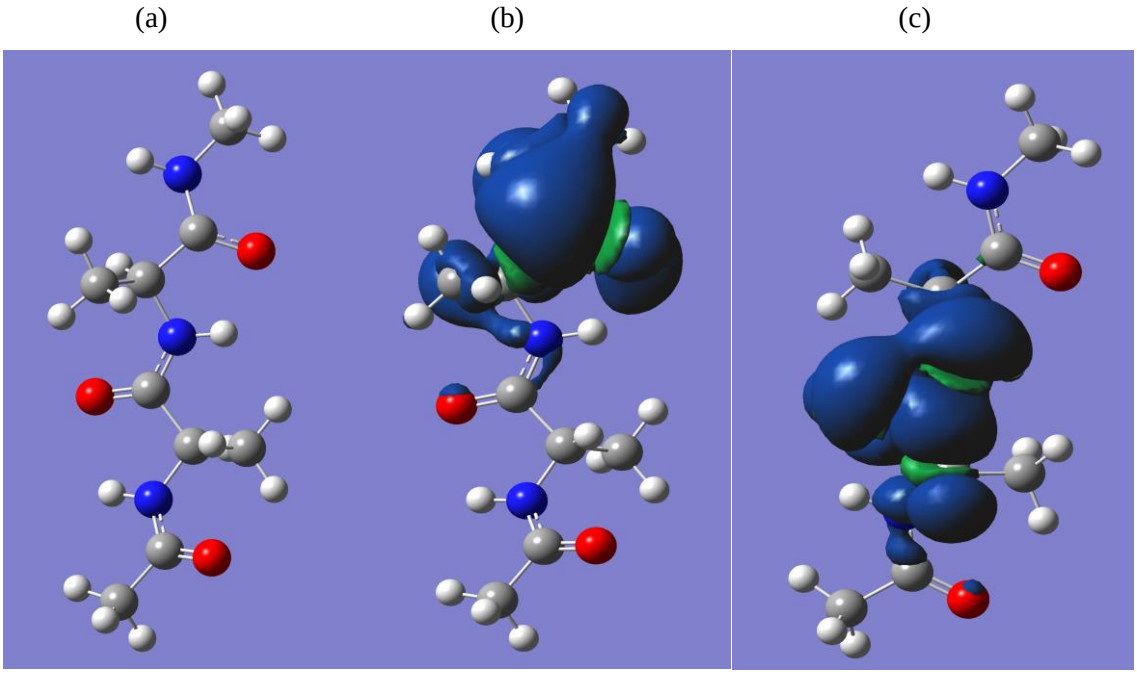

Figure S13 (a) The Ala-Ala model of the peptide backbone. (b) The radical anion with a majority of the spin density on the N-H end of the peptide. (c) The neutral radical formed by protonation of the radical anion (protonation is at the central C=O) majority with the spin density on this central >C=O.

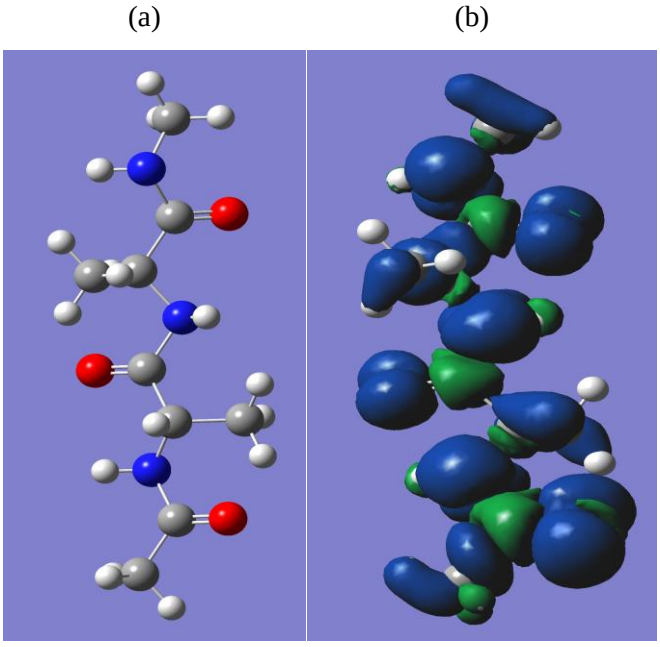

Figure S14 (a) The small peptide model (Ala-Ala). (b) Spin density of the cation radical

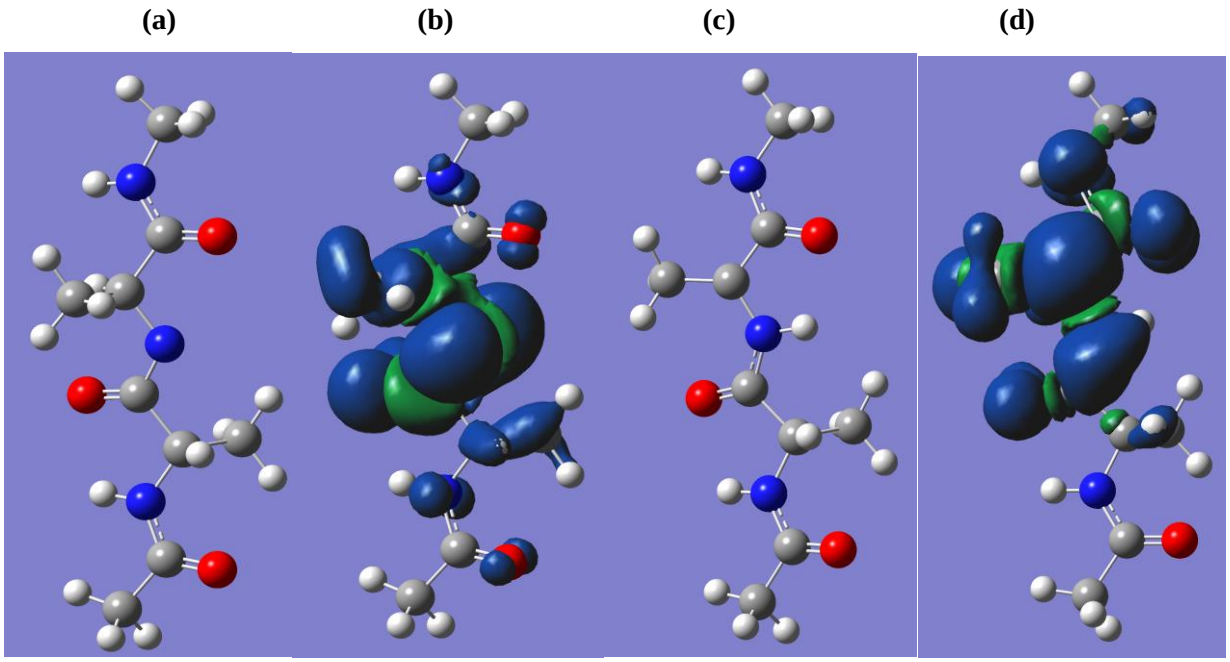

Figure S15 (a) The small peptide model (Ala-Ala) with deprotonation at the central nitrogen. (b) Spin density for this neutral radical 6.o2a in Scheme 6. (c) The small peptide model (Ala-Ala) with deprotonation at the central carbon. (d) Spin density for this neutral radical 6.o2b in Scheme 6.