**Supplemental material**

**Near-Threshold Electron Transfer in Anion-Nucleobase Clusters: Does the Identity of the Anion Matter?**

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S1 Higher-energy collisional dissociation (HCD) of the X-∙A (X-=I- and H2PO3-) anionic clusters

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**S1 Higher-energy collisional dissociation (HCD) of the X-∙A (X-=I- and H2PO3-) anionic clusters**

Higher-energy collisional dissociation (HCD) was performed to investigate the ground state fragmentation characteristics of the X-∙A (X-=I- and H2PO3-) anionic clusters. An Orbitrap Fusion Tribrid mass spectrometer (Thermo Fisher Scientific) with an ESI source was employed for these experiments and run in the negative ion mode. The instrument was operated at a flow rate of 5 μL/min. The following settings were used for both clusters: MS1 detector ion trap, MS1 maximum injection time, 100 ms; MS1 automated gain control (AGC) target, 100000; MS2 detector, ion trap; MS2 scan range, 50−600 MS2; AGC target, 100000; MS2 maximum injection time, 100: S-lens RF level, 50 V. As standard procedures [1-3], the HCD normalized collisional energy (the difference between the potential of the C-trap lenses and the ion routing multipole) was varied between 0 and 46 % (where 100 % is roughly 100 V), and the intensity of the ion in percentage was calculated.

In order to obtain a good cluster production, some parameters were slightly changed when analysing the two clusters H2PO3-·A (a) and I-·A (b):

1. Spray voltage, 2000 V; sweep gas flow rate, 1; sheath gas flow rate, 40; aux gas flow rate, 5; ion transfer tube temperature, 230°C; vaporizer temperature, 70°C.
2. Spray voltage, 2100 V; sweep gas flow rate, 1; sheath gas flow rate, 45; aux gas flow rate, 17; ion transfer tube temperature, 150°C; vaporizer temperature, 80°C.

H2PO3-, [A-H]- and PO3- are produced from H2PO3-·A, whilst I- is the only fragment produced by I-·A.



**Figure S1**: Fragment production curves for H2PO3-·A (a) and I-·A (b) upon HCD between 0 and 46 % energy

[1] Y. Zhang, S.B. Ficarro, S. Li and J.A. Marto, J. Am. Soc. Mass Spectrom. **20**, 1425 (2009).

[2] J.K. Diedrich, A.F.M. Pinto and J.R. Yates, J. Am. Soc. Mass Spectrom. 24, 1690 (2013).

[3] R. Cercola, E. Matthews and C.E.H. Dessent, J. Phys. Chem. B **121**, 5553 (2017).

**S2 TD-DFT transitions of X-∙A (X-=I- and H2PO3-)**

Figure 3 of the main text shows the TD-DFT spectra of the X-∙A (X-=I- and H2PO3-) clusters. The electronic transitions of the clusters, predicted by TD-DFT, are summarised in tables S1 and S2; including: transition assignments, transition energies and oscillator strengths.

The molecular orbitals involved in the electronic transitions predicted by TD-DFT calculations (performed at the B3LYP/6-311++G(2d,2p)/SDD on I) of the X-∙A7 (X-=I- and H2PO3-) clusters are presented in Figures S2 and S3.

According to these calculations, the transitions at 4.86 and 4.90 eV of the X-∙A cluster are coupled, more details in Table S1.

**Table S1** Calculated TDDFT transition energies and oscillator strengths of theI-·A (N7H) cluster. Calculations were performed at the B3LYP/6-311++G(2d,2p)/SDD level. Only transitions below 5.5 eV with oscillator strength > 0.005 are listed.

|  |  |  |
| --- | --- | --- |
| Orbital transitions | ∆E (eV) | f |
| (1.00)39(n)🡪40(π\*) | 3.78 | 0.0069 |
| (0.79)39(n)🡪41(σ\*) | 4.20 | 0.024 |
| (0.77)38(n)🡪41(σ\*) | 4.33 | 0.040 |
| (0.82)39(n)🡪42(σ\*) | 4.40 | 0.005 |
| (0.79)37(n)🡪41(σ\*) | 4.50 | 0.048 |
| (0.79)38(n)🡪42(σ\*) | 4.55 | 0.010 |
| (0.82)39(n)🡪44(σ\*) | 4.60 | 0.0090 |
| (0.82)37(n)🡪42(σ\*) | 4.68 | 0.0058 |
| (0.82)38(n)🡪44(σ\*) | 4.75 | 0.016 |
| (0.65)36(π)🡪40(π\*)  (0.18)37(n)🡪44(σ\*) | 4.86 | 0.15 |
| (0.65)37(n)🡪44(σ\*)  (0.19)36(π)🡪40(π\*) | 4.90 | 0.027 |
| (0.70)35(π)🡪40(π\*)  (0.26)36(π)🡪41(σ\*) | 5.01 | 0.0064 |
| (0.56)39(n)🡪45(π\*)  (0.36)39(n)🡪46(σ\*) | 5.18 | 0.091 |
| (0.60)38(n)🡪45(π\*)  (0.29)38(n)🡪46(σ\*) | 5.31 | 0.064 |
| (0.87)39(n)🡪47(π\*) | 5.42 | 0.011 |
| (0.60)37(n)🡪45(π\*)  (0.27)37(n)🡪46(σ\*) | 5.47 | 0.13 |
| (0.44)38(n)🡪46(σ\*)  (0.18)38(n)🡪45(π\*) | 5.50 | 0.011 |

   

**35 36 37** 38

   

**39 40 41 42**

   

**43 44 45 46**

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**47**

**Figure S2**: Molecular orbitals of I-·A involved in the transitions predicted by TDDFT calculations between 3.78 – 5.50 eV described in Table S1. The isovalue for each orbital surface is 0.02 e/au3 .

**Table S2** Calculated TDDFT transition energies and oscillator strengths of theH2PO3-·A (N7H) cluster. Calculations were performed at the B3LYP/6-311++G(2d,2p) level. Only transitions below 5.8 eV with oscillator strength > 0.005 are listed.

|  |  |  |
| --- | --- | --- |
| Orbital transitions | ∆E (eV) | f |
| (0.54)56(π)🡪58(phosphate σ\*)  (0.35)56(π)🡪59(σ\*) | 4.70 | 0.0052 |
| (0.84)56(π)🡪57(π\*) | 4.79 | 0.15 |
| (0.73)56(π)🡪62(π\*) | 5.13 | 0.0188 |
| (0.29)55(π)🡪58(phosphate σ\*)  (0.67)55(π)🡪59(σ\*) | 5.65 | 0.0566 |
| (0.57)54(π)🡪58(phosphate σ\*)  (0.21)54(π)🡪59(σ\*) | 5.81 | 0.0104 |
| (0.46)54(π)🡪57(π\*)  (0.21)56(π)🡪65(π\*) | 5.85 | 0.1676 |

   

**54**  **55 56 57**

   

**58 59 62 65**

**Figure S3**: Molecular orbitals of H2PO3-·A involved in the transitions predicted by TDDFT calculations between 4.70 – 5.85 eV described in Table S2. The isovalue for each orbital surface is 0.02 e/au3 .

**S3 Photofragment action spectrum of PO3- from H2PO3-·A**

The ion PO3- (m/z 79) is produced with a very low cross-section in the photodepletion experiment. Its photofragment action spectrum in shown in Figure S4.

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**Figure S4:** Photofragment action spectrum for PO3- that is produced from the H2PO3-·Acluster. The lines are five-point adjacent average of the data points.

**S4 Calculated Dipole Moments of X-∙A (X-=I- and H2PO3-)**

|  |  |  |
| --- | --- | --- |
| **Cluster** | **MP2 Dipole Detacheda**  Debye | **MP2**  **Dipole**  **Ground State**  Debye |
| I-∙A7 | 8.80 | 1.40 |
| I-∙A9 | 3.71 | 9.02 |
| I-∙A3 | 5.41 | 7.95 |
| H2PO3-∙A7 | 5.88 | 1.73 |
| H2PO3-∙A9 | 14.8 | 6.09 |
| H2PO3-∙A3 | 14.5 | 4.79 |

a Vertical dipole moments