Supporting Information: Dissociation of HCI in water nanoclusters: An energy decomposition analysis perspective

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Figure S1: Cluster geometries optimized at ω B97M-V/def2-TZVPD level of theory sorted by number of water molecules. The label indicates the cluster motifs, such as undissociated ring (**U**), aggregate (**A**), partial aggregate (**P**), solvent-separated ion pair (**S**), contact ion pair (**C**), and uncategorized (**X**). Additionally, the relative electronic energy (in kJ/mol) within each group is shown in parentheses. Particularly HCl(H₂O)₄ gives rise to a multitude of different cluster motifs.



Figure S2: Potential energy surface scan along the proton transfer coordinate $r_{\rm OH}$ for $\mathbf{X}_4^{3\rm u}$ at the $\omega \rm B97M-V/def2-TZVPD$ and RI-MP2/def2-TZVPD level of theory.

Dissociation



Figure S3: Relaxed potential energy surface scan of \mathbf{P}_{23}^{4u} along the proton transfer coordinate r_{OH} (level of theory: $\omega B97M$ -V/def2-TZVPD). The energy (blue) is given in kJ/mol relative to the equilibrium geometry of \mathbf{P}_{23}^{4u} (E_{eq}), whereas the H-Cl distance is shown in Å (green).



Figure S4: Interaction energy ΔE_{int} of \mathbf{P}_{23}^{4u} along the dissociation coordinate defined in Fig. S3. In addition to results from the full cluster (black), the plot also shows interaction energies for partial cluster geometries using one (blue), two (green) or three (orange) water molecules. The dotted vertical lines mark the equilibrium structures of \mathbf{P}_{23}^{4u} (blue) and \mathbf{C}_{6}^{4d} (red), respectively.



Figure S5: Frozen energy component $\Delta E_{\rm frz}$ along the dissociation coordinate of \mathbf{P}_{23}^{4u} defined in Fig. S3. In addition to results from the full cluster (black), the plot also shows energy components for partial cluster geometries using one (blue), two (green) or three (orange) water molecules. The dotted vertical lines mark the equilibrium structures of \mathbf{P}_{23}^{4u} (blue) and \mathbf{C}_{6}^{4d} (red), respectively.



Figure S6: Dispersion component ΔE_{disp} along the dissociation coordinate of \mathbf{P}_{23}^{4u} defined in Fig. S3. In addition to results from the full cluster (black), the plot also shows energy components for partial cluster geometries using one (blue), two (green) or three (orange) water molecules. The dotted vertical lines mark the equilibrium structures of \mathbf{P}_{23}^{4u} (blue) and \mathbf{C}_{6}^{4d} (red), respectively.



Figure S7: Polarization component $\Delta E_{\rm pol}$ along the dissociation coordinate of \mathbf{P}_{23}^{4u} defined in Fig. S3. In addition to results from the full cluster (black), the plot also shows energy components for partial cluster geometries using one (blue), two (green) or three (orange) water molecules. The dotted vertical lines mark the equilibrium structures of \mathbf{P}_{23}^{4u} (blue) and \mathbf{C}_{6}^{4d} (red), respectively.



Figure S8: Charge-transfer component ΔE_{ct} along the dissociation coordinate of \mathbf{P}_{23}^{4u} defined in Fig. S3. In addition to results from the full cluster (black), the plot also shows energy components for partial cluster geometries using one (blue), two (green) or three (orange) water molecules. The dotted vertical lines mark the equilibrium structures of \mathbf{P}_{23}^{4u} (blue) and \mathbf{C}_{6}^{4d} (red), respectively.



Figure S9: Difference of ALMO-EDA terms $(\Delta\Delta E = \Delta E(\mathbf{C}_6^{4d}) - \Delta E(\mathbf{P}_{23}^{4u}))$ in the dissociated and undissociated regime. In addition to results from the full cluster (black), the plot also shows $\Delta\Delta E$ components for partial cluster geometries using one (blue), two (green) or three (orange) water molecules.

Adiabatic ALMO-EDA

Table S1: Selected bond lengths (r) and angles (\measuredangle) of optimized \mathbf{X}_{18}^{4u} geometries corresponding to minima on the frozen (Frz), polarized (Pol), forward-CT (CTf), backward-CT (CTb) and fully relaxed potential energy surface (Tot). All interatomic distances are given in Å and bond angles are given in degree. The 2-fragment reference $(\text{HCl})((\text{H}_2\text{O})_4)$ was employed in the adiabatic ALMO calculations.

	\mathbf{Frz}	Pol	\mathbf{CTf}	\mathbf{CTb}	Tot
r(Cl-H1)	1.285	1.293	1.294	1.345	1.403
r(O1-H1)	2.282	2.063	2.045	1.623	1.448
r(Cl-H7)	3.336	3.102	3.139	2.928	2.708
r(Cl-H8)	2.902	2.751	2.533	2.683	2.373
r(O2-H2)	1.887	1.872	1.869	1.791	1.732
r(O3-H4)	1.842	1.841	1.839	1.818	1.799
r(O4-H6)	1.928	1.942	1.930	1.976	2.019
r(O4-H3)	2.297	2.265	2.284	2.197	2.163
\measuredangle (Cl-H1-O1)	155.0	160.0	158.6	170.8	170.8
∡(Cl-H7-O3)	130.0	128.6	138.4	126.1	139.6
∡(Cl-H8-O4)	115.5	120.6	119.4	123.7	131.5
∡(O1-H2-O2)	163.0	162.3	162.5	163.7	165.0
∡(O2-H4-O3)	166.5	164.9	165.4	162.8	161.4
∡(O3-H6-O4)	174.2	173.8	170.7	167.5	156.5
∡(O4-H3-O1)	133.2	137.5	135.2	137.8	134.8

Table S2: Selected bond lengths (r) and angles (\measuredangle) of optimized \mathbf{U}_{14}^{4u} geometries corresponding to minima on the frozen (Frz), polarized (Pol) and fully relaxed potential energy surface (Tot) as well as their respective differences Δ_1 and Δ_2 . All interatomic distances are given in Å and bond angles are given in degree. The 5-fragment reference, $(\text{HCl})(\text{H}_2\text{O})_4$, was employed in the adiabatic ALMO calculations.

	\mathbf{Frz}	Δ_1	Pol	Δ_2	Tot
r(Cl-H1)	1.283	0.006	1.289	0.066	1.356
r(O1-H1)	2.259	-0.200	2.058	-0.498	1.560
r(O2-H2)	2.198	-0.167	2.031	-0.332	1.699
r(O3-H4)	2.199	-0.164	2.035	-0.297	1.739
r(O4-H6)	2.209	-0.155	2.054	-0.277	1.777
r(Cl-H8)	2.825	-0.168	2.656	-0.355	2.301
∡(Cl-H1-O1)	176.3	1.1	177.4	1.3	178.7
∡(O1-H2-O2)	177.5	-1.4	176.1	2.7	178.8
∡(O2-H4-O3)	174.7	-0.5	174.2	1.9	176.1
∡(O3-H6-O4)	175.2	1.3	176.5	-0.7	175.8
∡(O4-H8-Cl)	173.3	-1.3	171.9	1.3	173.2

Table S3: Selected bond lengths (r) and angles (\measuredangle) of optimized \mathbf{P}_{23}^{4u} geometries corresponding to minima on the frozen (Frz), polarized (Pol) and fully relaxed potential energy surface (Tot) as well as their respective differences Δ_1 and Δ_2 . All interatomic distances are given in Å and bond angles are given in degree. The 5-fragment reference, (HCl)(H₂O)₄, was employed in the adiabatic ALMO calculations.

	\mathbf{Frz}	Δ_1	Pol	Δ_2	Tot
r(Cl-H1)	1.282	0.008	1.290	0.084	1.375
r(O1-H1)	2.363	-0.302	2.061	-0.552	1.509
r(O2-H2)	2.436	-0.183	2.253	-0.178	2.075
r(O2-H6)	2.429	-0.289	2.140	-0.197	1.943
r(O3-H3)	2.380	-0.169	2.210	-0.323	1.888
r(O4-H4)	2.282	-0.231	2.051	-0.277	1.774
r(Cl-H8)	3.146	-0.490	2.655	-0.384	2.271
∡(Cl-H1-O1)	146.0	21.3	167.3	8.7	176.0
∡(O1-H2-O2)	135.3	9.3	144.6	-4.5	140.1
∡(O1-H3-O3)	140.2	4.2	144.3	6.7	151.0
∡(O2-H6-O3)	139.2	14.8	153.9	-1.8	152.1
∡(O2-H4-O4)	138.8	25.5	164.3	1.9	166.2
∡(O4-H8-Cl)	139.4	26.3	165.7	0.2	165.9

Reference Bias

Fragment-based schemes require the definition of a reference, i.e. the group of atoms that make up each fragment. The result of such a fragment-based method, for instance the magnitude of the ALMO-EDA components, therefore intrinsically depends on the selected fragment reference. Furthermore the appropriate choice of fragments becomes less clear if chemical reactions are being studied. As new bonds are formed and others are broken, the initial choice of fragments may not be suitable anymore to describe the final molecular composition.

In order to demonstrate how the EDA components change with the choice of reference, the total frozen energy $E_{\rm frz}$ (including dispersion) was computed for three different fragment references along an effective proton transfer coordinate (r(OH)) for the smallest cluster $HCl \cdot H_2O(\mathbf{X}_1^{1u})$. The three chosen references consist of (a) undissociated fragments (termed $(HCl)(H_2O))$, (b) dissociated fragments involving a hydronium cation (termed $(Cl^-)(H_3O^+))$ and (c) dissociated fragments involving a proton fragment (termed $(H^+)(Cl^-)(H_2O))$). The corresponding geometries were obtained from a relaxed scan involving the fully relaxed wavefunction, whereby the distance between the acid-proton and the acceptor-oxygen (r(OH))was fixed for values between 0.9 and 4.0 Å. Note that the hydronium chloride complex is unstable in this system, i.e. the potential energy surface (PES) of the full system only has one minimum corresponding to the undissociated complex at $r_{\rm eq}(OH) = 1.895$ Å.

Figure S10 shows three frozen total energy curves along the effective proton transfer coordinate each in relation to the energy of non-interacting HCl and H₂O in the respective gas-phase equilibrium geometry, i.e. $E_{\text{lim}} = E_{\text{gas}}(\text{HCl}) + E_{\text{gas}}(\text{H}_2\text{O})$. We first consider the neutral reference (HCl)(H₂O). The corresponding frozen PES shows a minimum for an O-H distance of ca. 2.3 Å, which is about 0.4 Å longer than in the equilibrium geometry of \mathbf{X}_1^{lu} . Since the charge densities of the fragments were not yet allowed to polarize at the frozen level, it is expected that the inter-fragment separation is larger than in the equilibrium structure. For large r_{OH} the difference $E_{\text{frz}} - E_{\text{lim}}$ correctly approaches zero, whereas in



Figure S10: The frozen energy surfaces along the effective proton transfer coordinate for three fragment references. Each PES is presented in relation to the infinite separation limit $E_{\rm lim}$, i.e. the total energies of isolated H₂O and HCl in the gas-phase structure. The black crosses indicate the OH distance in the equilibrium structure of HCl·H₂O (1.895 Å).

the proton transfer regime $(r(OH) < r_{eq}(OH))$ the frozen energy becomes rapidly repulsive. This can be explained by the fact that once the hydronium cation is formed $(r(OH) \approx 1 \text{ Å})$, the neutral reference is no longer adequate and corresponds to a stretched HCl molecule in close proximity to a water molecule.

If instead the hydronium cation and chloride anion are chosen as a reference, the frozen energy is minimized at an OH distance of r(OH) = 0.95 Å, which is ca. 0.04 Å shorter as compared to the free hydronium cation. Whereas the ionic reference is an appropriate choice for the proton transfer regime, the frozen energy rises steeply for large values of r(OH) as the reference enforces a highly stretched OH bond in the hydronium fragment to the point where it can no longer be seen as a bond. The PES seems to approach an energy of ca. 900 kJ/mol above E_{lim} , which is about 200 kJ/mol more than the gas-phase proton transfer energy at the ω B97M-V/def2-TZVPD level of theory (685 kJ/mol).

The third choice of reference $((H^+)(Cl^-)(H_2O))$ is motivated by an attempt to remove the bias towards HCl or H₃O⁺ seen in the other two references by considering the proton as a separate fragment. Following this reference a hydronium cation and neutral HCl molecule are then treated on equal footing, however, it comes at the price of not being able to adequately describe the covalent bond on either end of the proton transfer. For instance, at the frozen level, the HCl molecule then closely resembles a chloride anion with a bare proton in close proximity. Using this three-fragment reference, the frozen energy is then minimized in a configuration where the proton is shared between the chloride and water fragment, i.e. r(OH) = 1.295 Å and r(HCl) = 1.420 Å, respectively. As neither the HCl nor the OH bond is formed at the frozen level, the position of the minimum can be attributed to maximising electrostatic interactions while minimizing Pauli repulsion between the three fragments.

Given that HCl dissociation does not occur for \mathbf{X}_{1}^{1u} , the neutral reference is the most reasonable choice among the three presented. Nevertheless, (HCl)(H₂O) as well as (Cl⁻)(H₃O⁺) are not universally applicable across the proton transfer coordinate, due to eventually breaking a bond within the fragment and forming of a new covalent bond between fragments. Based on the considerations above, we use a split approach, whereby undissociated and ionic clusters are investigated separately using a neutral and a $(Cl^-)(H_3O^+)$ -based reference, respectively. A reference involving a bare proton, e.g. $(Cl^-)(H^+)(H_2O)$, is used whenever undissociated and corresponding dissociated species demand a treatment on equal footing, for instance as part of a proton-transfer reaction path.

For HCl \cdot (H₂O)_n clusters with n > 1, it may be useful to treat some or all water molecules as a single fragment. As the water-water interactions within such a group will not be reflected in the interaction energy (and consequently neither in the EDA components), one can effectively isolate certain non-covalent interactions, for instance between HCl and the water cage ((HCl)(4 \cdot H₂O)).