ELECTRONIC SUPPLEMENTARY INFORMATION

Concerted proton migration along short hydrogen bonded water bridges in bipyridine/water clusters

Alexey Sergeevich Zatula[a], Mauritz Johan Ryding[a], and Einar Uggerud[a,*]

Abundance spectra

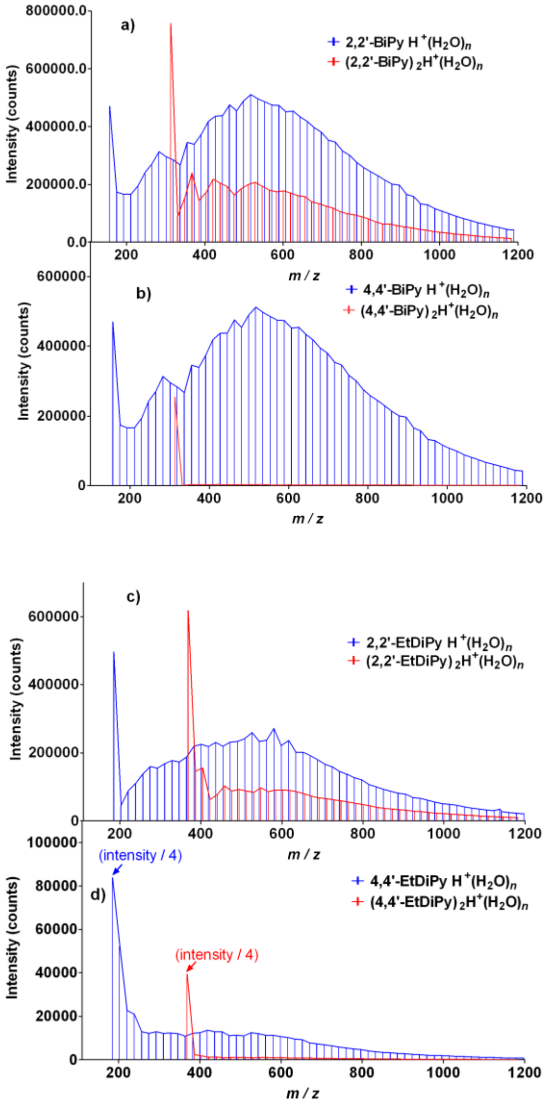


Figure S1(a–d). Abundance mass spectra obtained by electrospray ionization of aqueous solutions containing 5 mM 2,2’-bipyridine, 4,4’-bipyridine, 2,2’-ethylenebipyridine or 4,4’-ethylenebipyridine; the collision cell was empty. Lines between peaks are drawn only to guide the eye. The intensity of some peaks is reduced for clarity.

Fig. S1 provides cluster distributions of $MH^+(H_2O)_n$ obtained by electrospray ionization of corresponding aqueous solutions. While there are some intensity variations with size, no clear "magic numbers" can be seen. Molecule ions of each substance give strong signals in the spectra, while dimer ions M_2H^+ sometimes dominate the signal. In the spectrum of 4,4’-ethylenebipyridine, the intensity of the protonated monomer and dimer had to be decreased by a factor 4 for the sake of clarity. Dimer water clusters $M_2H^+(H_2O)_n$ are generally lower in intensity compared to $MH^+(H_2O)_n$ and are exceptionally low in case of the 4,4’-species.

Evaporation of H_2O

Figure S2 provides the amount of unimolecular decomposition of size-selected clusters $MH^+(H_2O)_n$ (M = 2,2’-BiPy, 4,4’-BiPy, 2,2’-EtBiPy or 4,4’-EtBiPy, $n \leq 30$) as a function of cluster size *n* during flight through the empty collision cell. The frequency of a water molecule loss is expressed as the ratio between peak corresponding to the evaporation product and the reactant ion abundance. The relative proportion of cluster ions that dissociate by loss of one single water molecule increases with cluster size in a nearly linear fashion for all species studied (Fig. S2). This linearity indicates that the evaporation rate from the clusters might be a function of cluster volume (*i.e.* the number of water molecules) as opposed to a surface dependence ($n^{2/3}$). Further inspection of Fig. S2 reveals that dramatic changes in evaporation rate with size—indicating magic numbers—are absent; the observed size variations are small.

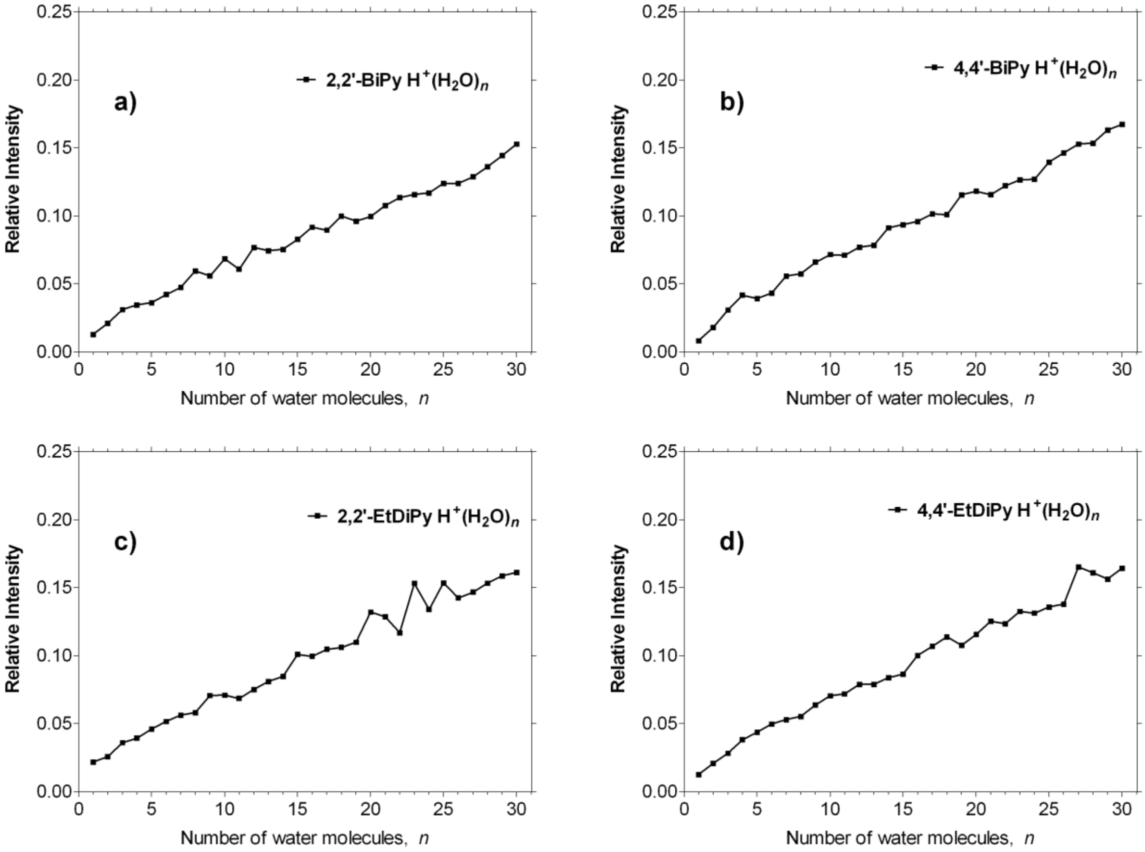
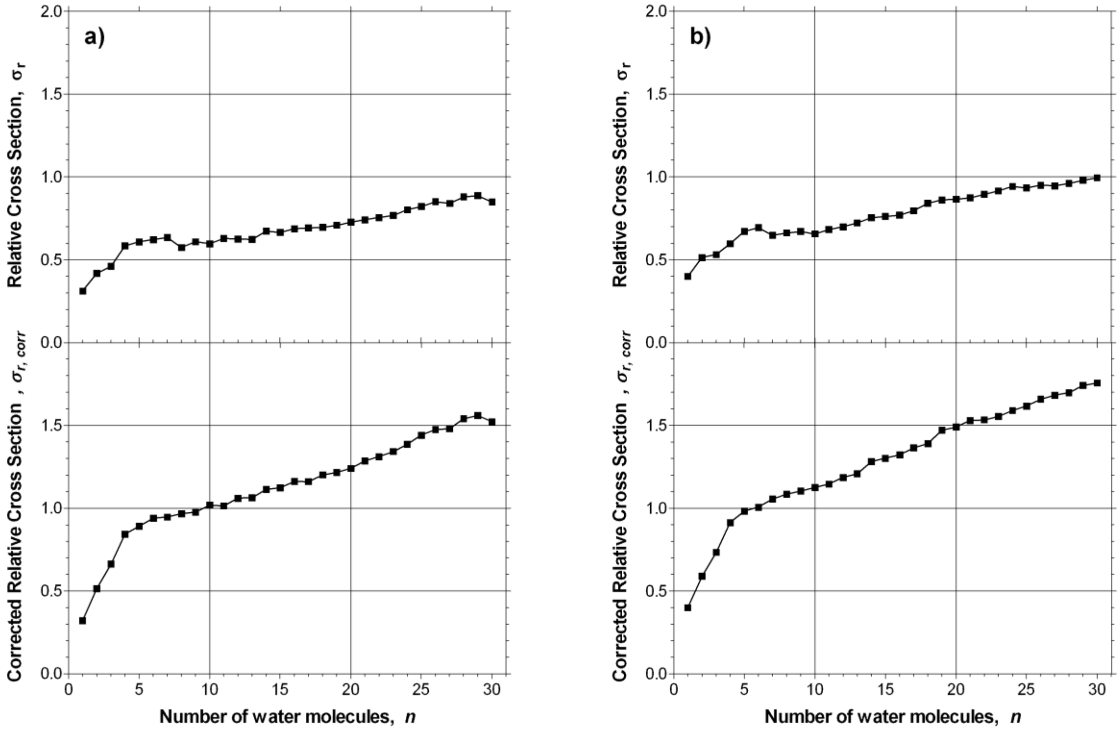


Figure S2 (a–d). The relative abundance of size-selected $MH^+(H_2O)_n$ clusters that evaporate one water molecule during passage through the empty hexapole collision cell. Panels correspond to: a) 2,2’-BiPy, b) 4,4’-BiPy, c) 2,2’-EtBiPy and d) 4,4’-EtBiPy.

Cross section for reaction with D_2O

The reaction of aqueous cluster ions with heavy water leads to products with masses that are one or two atomic mass units (u) greater than the reactant ion, depending on whether one or two protiums are exchanged for deuterium. The sum of the normalized intensities of the product peaks gives the fraction of exchange Φ for the cluster. The fraction of exchange is intimately linked to the cross section (σ) through a Lambert–Beer law analogy: $\sigma = -\ln(I/I_0)/(cL)$, where $I/I_0 = 1 - \Phi$, c is the concentration of D_2O, and L is the length of the collision cell. It should be noted that $-\ln(1 - \Phi) \approx \Phi$ as generally $\Phi \leq 0.1$. Since the D_2O pressure in the collision cell is not accurately known, it is not possible to obtain absolute cross sections for the reactions studied. However, by normalising to a reference cluster, it is possible to compare cross sections between different cluster types and experiments. This has been done, and the cross sections of protonated water clusters containing 2,2'-BiPy, 4,4'-BiPy, 2,2'-EtBiPy and 4,4'-EtBiPy are shown in the upper panels of Fig. S3a–d.

Due to spontaneous evaporation of water molecules after the reaction, some of the intensity is lost from the +1 u and +2 u product peaks. This can easily be corrected for, and the corrected cross sections are shown in the lower panels of Fig. S3a–d. The cross sections of $MH^+(H_2O)_n$ with M = 2,2'-BiPy, 4,4'-BiPy, shown in respectively Fig. S3a and Fig. S3b, exhibit a size dependence that is somewhere between linear and $n^{2/3}$ depending on the size region; with M = 2,2'-EtBiPy, 4,4'-EtBiPy (Fig. S3c–d) the size dependence is virtually absent in the current size range. The reason for this is unknown, but interesting.



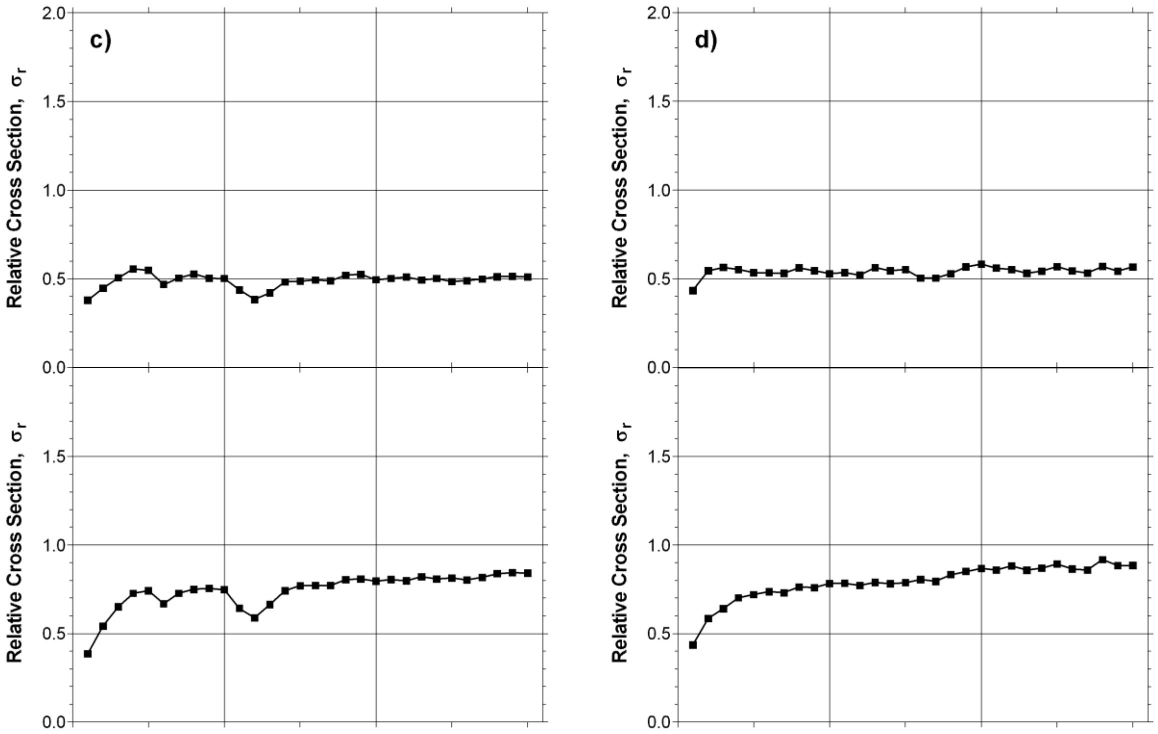


Figure S3. Relative cross sections and cross sections corrected for post-reaction loss of H_2O for clusters $MH^+(H_2O)_n$ reacting with D_2O at 0.1 eV centre-of-mass collision energy. a) M = 2,2’-BiPy, b) M = 4,4’-BiPy, c) M = 2,2’-EtBiPy and d) M = 4,4’-EtBiPy. The cross sections are all expressed relative to the uncorrected cross section of a reference cluster, $H^+(H_2O)_{11}$, that was averaged over each experiment.

Computational details

Quantum chemical calculations were carried out using the program system GAUSSIAN 09 [1]. All structures water clusters structures $A(H_2O)_2$ (A = 2,2’-BiPy, 2,2’-EtBiPy, and 4,4’-EtBiPy) were characterised by complete geometry optimisation using the range corrected version of the popular hybrid density functional CAM-B3LYP [2] [37], in conjunction with the aug-cc-pVDZ basis [2,3].

1. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, in, Wallingford CT, 2009.

2. T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett., 2004, 393, 51-57.

3. N. Bork, T. Kurtén, M. B. Enghoff, J. O. P. Pedersen, K. V. Mikkelsen and H. Svensmark, Atmos. Chem. Phys., 2011, 11, 7133-7142.

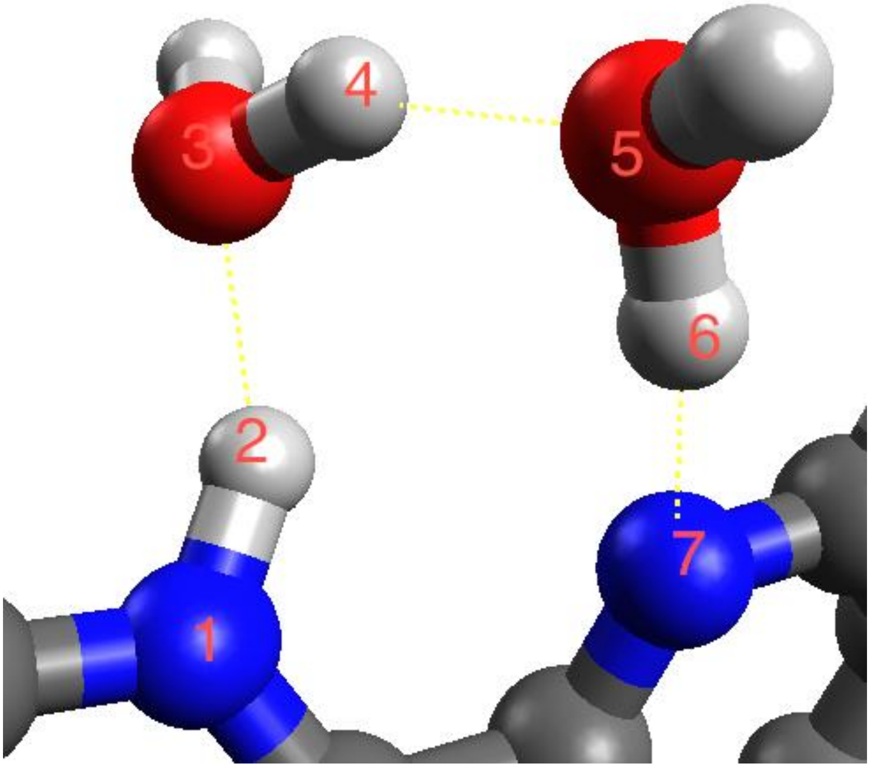


Table S1. Selected bond lengths (Å) and angles (degrees) computed for water bridges using CAM-B3LYP/aug-cc-pVDZ.

	2,2'-BiPyH$^+$(H$_2$O)$_2$	2,2'-EtBiPyH$^+$(H$_2$O)$_2$	4,4'-EtBiPyH$^+$(H$_2$O)$_2$
N1-H2, A	1.046	1.063	1.048
H2-O3, A	1.720	1.572	1.656
N1-H2-O3	149.9	174.7	150.7
O3-H4, A	0.988	0.996	0.988
H4-O5, A	1.746	1.609	1.723
O3-H4-O5	152.1	168.1	170.4
O5-H6, A	0.979	0.998	0.985
H6-N7, A	1.975	1.731	1.859
O5-H6-N7	154.3	173.1	161.6
N1-N7, A	2.794	5.012	4.434