Supplementary Information:

Experimental and theoretical evidence of charge transfer in weakly bound complexes of water

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Details of the calculations

All calculations have been carried out at the coupled cluster level of theory[1] with single, double, (CCSD) and perturbatively included triple excitations (CCSD(T)) using augmented correlation consistent polarized valence basis sets up to quintuple-zeta (**aug-cc-pVxZ** with x=D, T, Q, 5).[2] In the case of the He, Ne, and Ar complexes a single point energy calculation using the sextuple-zeta aug-cc-pV6Z basis set[3] has been carried out at the geometry optimized with the aug-cc-pV5Z basis. We shall refer to these basis sets as AVxZ, with x=D, T, Q, 5, 6. For the heavier Xe atom, relativistic effects have been taken into account through the use of small-core pseudopotentials[2]. All the ab-initio calculations have been carried out using the program MOLPRO.[4]

We have investigated in detail, on all the molecules, the basis set convergence for the determination of both the lowest-energy nuclear arrangement and the corresponding energy of interaction. The equilibrium geometries have been determined by performing geometry optimizations at the CCSD(T) level. The Ng-water complexes are known to be planar (see, e.g., Ref. 5 and references therein), so the geometry optimizations have been constrained accordingly. We have confirmed the results of previous works that the interaction with a noble gas leaves the geometry of free water essentially unaffected[5] and that the change in the interaction energy due to water geometry relaxation is negligible. For example, we find in the Ar-H₂O adduct that the O-H distances vary by less than 0.001 Å, and the H-O-H angle by less than 0.2 degrees. For this reason, the water molecule has been kept rigid at its free equilibrium structure[6] during the geometry optimizations.

The basis set superposition error (BSSE) for the Ng-water interaction energy was evaluated for all complexes using the counterpoise correction of Boys and Bernardi.[7] The analysis of the electron density and the charge transfer have been carried out using the CCSD relaxed density.[8]

A natural bond orbital (NBO) analysis[9] was performed, using Gaussian03 [10]. These calculations have been performed at the CCSD level using the AVDZ, AVTZ, and AVQZ basis sets.

In the case of Ar-H₂O, Symmetry-Adapted Perturbation Theory (SAPT) calculations[11] using the SAPT2008 program.[12] The calculations have been performed in the DCBS scheme[12] at the intra-monomer CCSD level using the aug-cc-pVQZ basis set. Using SAPT we have also optimized the complex geometry under the same constraints explained abovee.

Geometry optimizations

The optimized geometrical parameters for the Ng-water complexes obtained with various basis sets are reported in Table I. The molecular structure is characterized by the Ng-O distance r and the angle Φ between the Ng-O axis and the water symmetry axis. $\Phi = 0$ corresponds to Ng approaching between the hydrogen atoms. The various basis sets give

TABLE I: Computed geometrical parameters of the Ng-H₂O complexes at the CCSD(T) level with different basis sets. r is in Å, Φ is in degrees.

	He-H ₂ O		$Ne-H_2O$		$Ar-H_2O$		Kr-H ₂ O		$Xe-H_2O$	
Basis	r	Φ	r	Φ	r	Φ	r	Φ	r	Φ
AVDZ	3.10	101.8	3.39	72.1	3.71	64.4	3.83	62.1	4.02	60.1
AVTZ	3.19	93.4	3.33	63.6	3.64	63.0	3.78	58.8	3.90	59.4
AVQZ	3.10	108.6	3.32	75.4	3.66	66.0	3.84	60.9	4.00	59.6
AV5Z	3.16	97.1	3.35	82.0	3.67	67.1	3.84	61.6	4.02	61.2

very similar geometries. The largest deviations are seen for the He and Ne complexes, where the interaction energy is significantly smaller than in the heavier molecules (see below), and the potential energy surface flatter. The SAPT/AVQZ calculations yield the equilibrium geometry for Ar-H₂O as r = 3.70 Å, $\Phi = 65.4$ degrees.

Study of the interaction energy

Table II reports the Ng-water interaction energies computed with various basis sets and the two Coupled Cluster levels at the complex geometries optimized at the CCSD(T)/AV5Zlevel. The interaction energy is given as the energy difference between a calculation on the complex and separate calculations on the isolated fragments. The table shows that obtaining accurate interaction energies for these weakly bound systems requires very large basis sets: convergence in the BSSE-corrected results only begins to set in (to within about 10%) with

		He-H ₂ O		Ne-H ₂ O		Ar-H ₂ O		Kr-H ₂ O		Xe-H ₂ O	
Basis	Method	Е	BSSE								
AVDZ	CCSD	0.532		1.008		2.028		2.570		2.656	
	$\operatorname{CCSD}(T)$	0.602	0.234	1.226	0.377	2.458	0.774	3.104	0.979	3.307	1.003
AVTZ	CCSD	0.398		1.146		1.970		2.229		2.551	
	$\operatorname{CCSD}(T)$	0.474	0.351	1.332	0.623	2.476	1.426	2.807	1.755	3.250	2.046
AVQZ	CCSD	0.357		0.949		1.534		1.765		1.930	
	$\operatorname{CCSD}(T)$	0.436	0.391	1.137	0.681	2.042	1.619	2.344	1.942	2.622	2.314
AV5Z	CCSD	0.344		0.678		1.417		1.617		1.783	
	$\operatorname{CCSD}(\mathrm{T})$	0.424	0.404	0.872	0.730	1.929	1.659	2.194	1.981	2.471	2.295
AV6Z	CCSD	0.337		0.616		1.310					
	$\operatorname{CCSD}(T)$	0.417	0.408	0.808	0.742	1.814	1.674				

TABLE II: Computed interaction energy E (kJ/mol) of the Ng-H2O complexes. For the CCSD(T) calculations the energy corrected for basis set superposition error (BSSE) is also reported.

the AVQZ basis sets. If BSSE is neglected, the computed interaction energy decreases with increasing basis set size, but when BSSE is taken into account the trend reverses and the estimated energy actually increases. There is a clear pattern of significant increase of the interaction energy upon including triple excitations in the Coupled Cluster expansion, clearly indicating the large role played by electron correlation. Remarkably, this increase is found to be, for each molecule, nearly constant regardless of the basis set used. BSSE is unacceptably large with the smaller basis sets and in some cases, Ne-H₂O and Ar-H₂O, is still a non-negligible fraction of the binding energy with the large AV5Z basis. Since BSSE invariably reduces the estimated dissociation energy, with intermediate basis sets the effect of triple excitations and BSSE tend to cancel each other out to a remarkable extent. For comparison, the SAPT/AVQZ interaction energy of Ar-H₂O at its own optimal geometry (see above) is computed to be 1.742 kJ/mol. The corresponding energy decomposition is shown in Fig. 1, along with that computed for two other arrangements of the complex, at $\Phi = 0$ and $\Phi = 180^{\circ}$ respectively.

Charge transfer analysis

In Fig. 2 we report the $\Delta q(z)$ charge-transfer curves (see the main text) for the Ar-H₂O system obtained with the CCSD method and three different basis sets: AVDZ, AVTZ, and AVQZ. The figure shows that the observed pattern of charge transfer along the Ng-O axis is



FIG. 1: SAPT/AVQZ energy decomposition for the complex Ar-H₂O at three stationary points on the energy surface characterized by different angles of approach Φ (see text). For the definition of the various energy terms, see Refs. 11, 12 and references therein.

largely independent of the basis set and it is in fact essentially quantitatively identical with the AVTZ or larger basis set.

In Table III we report the NBO charges for the Ng-H₂O and Ne-Ar complexes with various basis sets at the respective equilibrium geometries.

Study of charge transfer at various geometries

In Fig. 3 we show the CCSD/VQZ density difference contour plots and charge-transfer curves for a series of different orientations of the Ar-H₂O complex. The sole Δq curves for several other coplanar orientations of the Ar-H₂O complex are collected in Fig. 4.

In Fig. 5 we show the charge transfer for different orientations of the $Ar-H_2O$ binary complex obtained with the NBO polulation analysis at the CCSD/AVQZ level.



FIG. 2: Charge-transfer curves for the Ar-H₂O binary complex obtained from the CCSD relaxed electron density with three different basis sets.

	$\mathrm{He}\text{-}\mathrm{H}_{2}\mathrm{O}$	$Ne-H_2O$	Ar-H ₂ O	$\mathrm{Kr} ext{-}\mathrm{H}_2\mathrm{O}$	$Xe-H_2O$	Ne-Ar
Basis						
AVDZ	0.24	1.12	3.45	4.00	4.73	-0.02
AVTZ	0.33	0.95	2.85	3.14	3.99	0.00
AVQZ	0.44	1.11	3.32	3.56	4.31	0.00

TABLE III: Computed CCSD/NBO charges of the Ng- H_2O and Ne-Ar complexes with different basis sets. The charges (in me) are positive on on the Ng atom (on Ne in Ne-Ar).

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FIG. 3: CCSD/VQZ contour plots of the electron density changes and charge-transfer curves for different orientations of the Ar-H₂O binary complex. Φ is the angle between the Ar-O axis and water's C_2 symmetry axis in the coplanar arrangement. $\Phi = 0$ corresponds to Ar approaching between the hydrogen atoms, $\Phi = 180$ is the opposite orientation with Ar facing the oxygen atom, and $\Phi = 67$ is the computed equilibrium geometry of the complex. The label "TOP" denotes an out-of-plane configuration with Ar placed on the perpendicular through O to the water plane. Each configuration is on a stationary point of the electronic potential energy surface.



FIG. 4: CCSD/VQZ charge-transfer curves for different orientations of the Ar-H₂O complex in the coplanar arrangement. Φ is the angle between the Ar-O axis and water's C_2 symmetry axis. $\Phi = 0$ corresponds to Ar approaching on the hydrogen side.



FIG. 5: Charge transfer in the NBO population analysis for different coplanar orientations of the Ar-H₂O binary complex computed at the CCSD/AVQZ level. Φ is the angle between the Ar-O axis and water's C_2 symmetry axis. $\Phi = 0$ corresponds to Ar approaching on the hydrogen side. The charge reported (in me) is that on the Ar atom.

- a) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, 157, 479; b) C. Hampel, K. A. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, 190, 1; c) M. J. O. Deegan, P. J. Knowles, *Chem. Phys. Lett.* **1994**, 227, 321.
- [2] a) T. H. Dunning, J. Chem. Phys. 1989, 90, 1007; b) D. E. Woon, T. H. Dunning, J. Chem. Phys. 1994, 100, 2975; c) D. E. Woon, T. H. Dunning, J. Chem. Phys. 1993, 98, 1358; d) K. A. Peterson, D. Figgen, E. Goll, H. Stoll, M. Dolg, J. Chem. Phys. 2003, 119, 11113.
- [3] a) A. K. Wilson, T. van Mourik, T. H. Dunning, J. Mol. Struct. Theochem 1996, 388, 339;
 b) K. A. Peterson, D. E. Woon, http://gnode2.pnl.gov.
- [4] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, and others, Molpro version 2006.1, a package of ab initio programs, see http://www.molpro.net.
- [5] a) J. Makarewicz, J. Chem. Phys. 2008, 129, 184310; b) L. Wang, M. Yang, J. Chem. Phys. 2008, 129, 174305.
- [6] E. M. Mas, K. Szalewicz, J. Chem. Phys. 1996, 104, 7606.
- [7] S.F. Boys, F. Bernardi, Mol. Phys. 1970, 19, 553.
- [8] a) T. Korona, R. Moszynski, B. Jeziorski, Mol. Phys. 2002, 100, 1723; b) T. Korona, B. Jeziorski, J. Chem. Phys. 2006, 125, 184109.
- [9] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* 1988, *88*, 899; b) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *"NBO 5G"* (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001); see http://www.chem.wisc.edu/ nbo5.
- [10] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V.

Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko,
P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng,
A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C.
Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

- [11] B. Jeziorski, R. Moszynski, K. Szalewicz, Chem. Rev. 1994, 94, 1887;
- [12] R. Bukowski, W. Cencek, P. Jankowski, M. Jeziorska, B. Jeziorski, S. A. Kucharski, V. F. Lotrich, A. J. Misquitta, R. Moszyński, K. Patkowski, R. Podeszwa, S. Rybak, K. Szalewicz, H. L. Williams, R. J. Wheatley, P. E. S. Wormer, P. S. Żuchowski, SAPT2008: An Ab Initio Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interaction Energies. Sequential and parallel versions. User's Guide, see http://www.physics.udel.edu/~szalewic/SAPT/SAPT.html.