

Molecular Cluster Bowl To Enclose a Single Electron

Kwang S. Kim,* Sik Lee, Jongseob Kim, and Jin Yong Lee

Department of Chemistry and Center
for Biofunctional Molecules
Pohang University of Science and Technology
San 31, Hyojadong, Namgu, Pohang 790-784, Korea

Received April 18, 1997

Revised Manuscript Received June 11, 1997

It is exciting if a single electron can be enclosed in a container (as if a guest in a host molecule)¹ and be manipulated by a tweezer-like tool. With hope to find such a fascinating structure, we have undertaken state-of-the-art ab initio calculations of a partially hydrated electron system which has been speculated as an internally localized excess-electron state.² We indeed find that an electron can be trapped/held in a bowl/tweezer-like cluster comprised of six water molecules and that the gates/arms formed by two water molecules can control the electron transfer process. It is of interest to note that some spectra of the species have already been observed in brilliant experiments (the first mass spectra by Haberland group,^{2,3} the first photoelectron spectra by Bowen group,^{2,4} the first Rydberg electron transfer study by Schermann group,^{4,5} the first vibrational autodetachment spectra by Johnson group,^{6,7} etc.), while its novel structure and fascinating characteristics are unknown. These exciting features together with the existing studies of electron bound to molecular clusters^{1–10} could be of immense interest and profound value in studies ranging from electron release and trapping to transport phenomena.

To investigate an internally localized excess-electron state, we have studied a partially hydrated electron system: $e^+(\text{H}_2\text{O})_6$. An exhaustive search for all of the low-lying energy structures has been done in a systematic and logical approach.¹¹ Finally, we obtained eight representative low-lying energy conformers

(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Germany, 1995. (b) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: England, 1994.

(2) (a) Coe, J. V.; Lee, G. H.; Eaton, J. G.; Arnold, S. T.; Sarkas, H. W.; Bowen, K. H.; Ludewigt, C.; Haberland, H.; Worsnop, D. R. *J. Chem. Phys.* **1990**, *92*, 3980. (b) Lee, G. H.; Arnold, S. T.; Eaton, J. G.; Sarkas, H. W.; Bowen, K. H.; Ludewigt, C.; Haberland, H. *Z. Phys. D* **1991**, *20*, 9.

(3) Haberland, H.; Ludewigt, C.; Schindler, H.-G.; Worsnop, D. R. *J. Chem. Phys.* **1984**, *88*, 3742.

(4) Desfrancois, C.; Khelifa, N.; Lisfi, A.; Schermann, J. P.; Eaton, J. G.; Bowen, K. H. *J. Chem. Phys.* **1991**, *95*, 7760.

(5) Desfrancois, C.; Lisfi, A.; Schermann, J. P. *Z. Phys. D* **1992**, *24*, 297.

(6) Campagnola, P. J.; Cyr, D. M.; Johnson, M. A. *Chem. Phys. Lett.* **1991**, *181*, 206.

(7) Bailey, C. G.; Kim, J.; Johnson, M. A. *J. Phys. Chem.* **1996**, *100*, 16782.

(8) (a) Knapp, M.; Echt, O.; Kresle, D.; Recknagel, E. *J. Chem. Phys.* **1986**, *85*, 636. (b) Misaizu, F.; Kondow, T.; Kuchitsu, K. *Chem. Phys. Lett.* **1991**, *178*, 369.

(9) (a) Barnett, R. N.; Landman, U.; Scharf, D.; Jortner, J. *Acc. Chem. Res.* **1989**, *22*, 350. (b) Kim, J.; Park, J. M.; Oh, K. S.; Lee, J. Y.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **1997**, *106*, 10207. (c) Chandler, D.; Leung, K. *Ann. Rev. Phys. Chem.* **1994**, *45*, 557. (d) Schwarz, B. J.; Rosky, P. J. *J. Phys. Chem.* **1995**, *99*, 2953. (e) Deng, Z.; Martyna, G. J.; Klein, M. *Phys. Rev. Lett.* **1993**, *71*, 267. (f) Miura, S.; Hirata, F. *J. Phys. Chem.* **1994**, *98*, 9649.

(10) (a) Kim, K. S.; Park, I.; Lee, S.; Cho, K.; Lee, J. Y.; Kim, J.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1996**, *76*, 956. (b) Lee, S.; Lee, S. J.; Lee, J. Y.; Kim, J.; Kim, K. S.; Park, I.; Cho, K.; Joannopoulos, J. D. *Chem. Phys. Lett.* **1996**, *254*, 128.

(11) We considered various topologically different conformers comprised of six water monomers (752 conformers classified into 39 distinctive types) and several zwitterionic conformers. Among these, 28 possible low-lying energy conformers were selected for investigation using high-level ab initio calculations. For further extensive investigation, eight representative conformers were then chosen on the basis of their relative energies and topological characteristics. For more calculational details see: Lee, S.; Kim, J.; Lee, S. J.; Kim, K. S. *Phys. Rev. Lett.* **1997**, *97*, 2038.

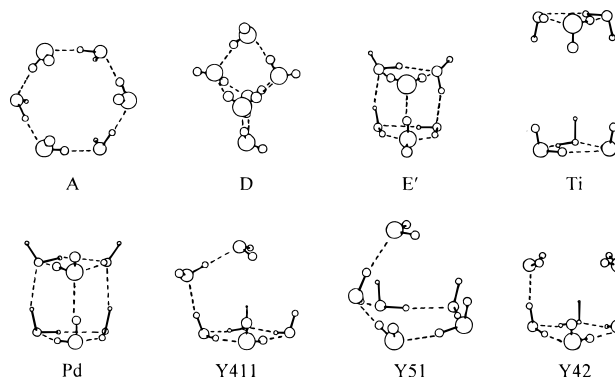


Figure 1. Possible low-lying energy conformers.

(Figure 1): three surface states (A, D, E'), one internal state (Ti), one dipole-bound surface state (Pd), three hybrid (i.e., partially internal and partially surface) states (Y411, Y51, Y42).¹² The Möller–Plesset second-order perturbation (MP2) theory using the 6-311++G** basis set was performed with full geometry optimization.¹³ Vibrational frequencies and zero-point energies (ZPEs) were obtained with density functional calculations employing Becke–Lee–Yang–Parr (BLYP) type nonlocal density functional¹⁴ and using the 6-311++G** basis set. The most stable structure is then Y42, followed by Y51 and Y411 (Table 1). This was further verified by MP2 calculations with 6-311++G(2df,2p)+diffuse(sp/d) at the MP2/6-311++G**-optimized geometries.¹⁵ Therefore, the hybrid-state structures with highly clustered dangling hydrogen atoms (H_d s) and large dipole moments tend to be very stable due to the combined $e^{\bullet\bullet}\text{H}_d$ and $e^{\bullet\bullet}$ dipole interactions. Thus, these combined interactions would help guide electron pathways.

Our predicted lowest-lying energy structures corresponding to two strong experimental VDE peaks^{7,16} of 0.47 eV and 0.18 eV are Y42 (0.46 eV) and Y51 (0.16 eV). Y411 and Pd have VDEs of 0.28 and 0.06 eV, which correspond to both ends of the broad band⁷ (0.07–0.30 eV) with a peak of 0.18 eV. Since the intensity is stronger with increasing structural stability, our predicted structures explain well the experimental relative spectral intensities.^{2,7} We also investigated strong O–H stretching vibrational frequencies. Among the conformers studied above, the minimum-energy structure Y42 (in which the red-shifts of the O– H_d frequencies are 370 and 271 cm^{-1} by MP2/6-31++G* and 398–382 and 358 cm^{-1} by BLYP/6-311++G**) conforms to two strong peaks of Bailey et al.'s vibrational autodetachment spectra⁷ (3268 and 3378 cm^{-1} which are red-shifted by ~ 450 and ~ 340 cm^{-1} relative to the free O–H stretching frequencies). The O–H stretching frequencies involved in $e^{\bullet\bullet}\text{H}_d$ interactions are red-shifted by 100–500 cm^{-1} , which is similar to the values involved in hydrogen bonding (which is much weaker than covalent bonding). This indicates

(12) Notations “T” and “P” denote triangular-rings and prism, respectively, and “Y” denotes a hybrid state with highly clustered dangling H atoms and large dipoles (Y42 represents a four-membered ring with two arms); “i” and “d” denote internal and dipole-driven states, respectively.

(13) Frisch, M. J.; et al. *Gaussian 94*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1995.

(14) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) The exponents of the diffuse functions for O are 0.017 for the first set of s and p functions, 0.003 for the second set, and 0.08 for the d function, while that for H is 0.05 for the p function.

(16) The first experimental values for these VDEs (~ 0.5 and ~ 0.2 eV) were reported by Bowen, Haberland, and collaborators.²

(17) Red-shifts of strong IR peaks by BLYP/6-311++G** (in cm^{-1}): Y51 (433–390, 271–252, 152–122); Y411 (444–418, 248–205, 176–143); Pd (341–330, 230); Ti (250–225). Red-shifts of IR peaks for Y42 are found at 133 and 124 cm^{-1} , which confirms a very recent experiment: Bailey, C. G.; Ayotte, P.; Kim, J.; Johnson, M. A. *Recent Theoretical Advances in Hydrogen-Bonded Clusters*; NATO Adv. Inst.: Crete, Greece, 1997.

Table 1. Relative ZPE-Corrected Energies (kcal/mol) and VDEs (eV) of Anionic Water Hexamers and Dipole Moments (debyes) of the Corresponding Neutral Species at the Optimized Anionic Geometries^a

	A	D	E'	Ti	Pd	Y411	Y51	Y42
MP2/6-311++G**								
ΔE_0	5.11	6.61	4.83	7.37	2.71	1.60	1.44	0.00
VDE	-0.24	-0.53	-0.39	0.45	0.06	0.28	0.16	0.46
μ_{neut}	0.00	4.67	4.59	0.00	10.72	8.20	7.72	9.35
MP2/611++G(2df,2p) + diffuse(sp/d,p)/MP2/6-311++G**								
ΔE_0						1.32	0.74	0.00

^a The ZPE correction was done with the DFT/6-311++G** frequencies.

that the excess electron would exist, to a certain extent, nearly freely in the bowl/tweezer of Y42 having little interaction with the bowl/tweezer chemically.

The lowest-energy structure Y42 can trap a single electron in its bowl, as seen from its HOMO in Figure 2. When the excess electron is detached from Y42 in an instant, it is structurally transformed to a local minimum energy structure of the neutral state G_0 via an intermediate neutral state $Y42_o^*$ (Figure 2), where subscript "o" denotes a neutral state. At the MP2/6-311++G(2df,2p)+diffuse(2s2pd/p) level,¹⁵ the anionic structure Y42 is 0.6 kcal/mol lower in ZPE-corrected energy (ΔE_0) than the neutral structure G_0 . On opening the gate of the bowl/tweezer structure (Y42), the excess electron is released through the vacant space between dangling H_{4s} . As a result, the bowl/tweezer-like Y42 is transformed into a wide-open gate structure (G_0).¹⁸⁻²¹ As seen from the excess electron density distribution changes, electron transfer process through the passage surrounded by four H_{4s} of the two water molecules above the four-membered ring demonstrates that a novel through-space (as opposed to the through-bond one) would be possible in biomolecular systems (e.g., an azuline dimer²² having Cu(I) and Cu(II) redox centers bridged by two water molecules). This concept could be utilized to transport electrons in condensed matter and biomolecular systems via H_4 -surrounded pathways by controlling orientations of H_{4s} .

(18) The energy barrier for the transformation of Y42 to G_0 would be low (only a few kcal/mol), because it would be lower than the intersection of the two potential wells representing the energy profiles of the anionic state around Y42 (VDE 11 kcal/mol) and the neutral state around G_0 (vertical electron affinity -19 kcal/mol). On the other hand, the lowest-lying energy conformers of the neutral state (corresponding to A, D, E', and open book shape)^{19,20} are 2.3 and 1.7 kcal/mol lower in ΔE_0 than G_0 and Y42, respectively; (the neutral state corresponding to D was recently identified in exquisite experiment by Saykally and collaborators).²⁰ However, owing to transition barriers (to require partial hydrogen-bonding formation or breaking),²¹ G_0 and Y42 may not be transformed easily to the neutral conformers of the lowest-lying energies.

(19) (a) Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451. (b) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41. (c) Franken, K. A.; Jalaie, M.; Dykstra, C. E. *Chem. Phys. Lett.* **1992**, *198*, 59. (d) Mhin, B. J.; Kim, J.; Lee, S.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1994**, *100*, 4484. (e) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.

(20) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501.

(21) The water-water hydrogen-bonding energy is ~ 5 kcal/mol. See, for example: Kim, K. S.; Mhin, B. J.; Choi, U.-S.; Lee, K. *J. Chem. Phys.* **1992**, *97*, 6649.

(22) Nar, H.; Messerschmidt, A.; Huber, R.; van de Kamp, M.; Canters, G. W. *J. Mol. Biol.* **1991**, *218*, 427.



Figure 2. Electron density distributions of HOMO for the initial electron-containing structure Y42 (top) and LUMO for a structure of an intermediate electron-released neutral-state $Y42_o^*$ (middle), and the structure of the final neutral-state G_0 , upon detaching the excess electron from Y42 in an instant (bottom). The $Y42_o^*$ is one of the conformers obtained during the energy minimization process after detaching an electron from Y42. The HOMO of Y42 and LUMO of $Y42_o^*$ are very similar to the LUMO of the electron-released neutral state at the Y42 geometry and the HOMO of the electron-containing anionic state at the $Y42_o^*$ geometry, respectively.

In summary, the lowest energy structure Y42 is the first molecular cluster bowl/tweezer to hold a single electron, the release, capture, and transport of which might be controlled by the gate/arm mechanism. The present concept to control a single electron in a molecular system should provide a new insight into the design of novel hosts capable of capturing/releasing and transporting guests in host-guest molecular recognition chemistry. The elucidation of the novel structure, novel interactions to guide an electron or to govern electron pathways, and fascinating characteristics of the system in conjunction with the illuminating experiments²⁻⁷ may open up new vistas in science.

Acknowledgment. This work was supported in part by KOSEF/CBM, KOSEF (96-05-01-02-01-3), Korea Research Foundation, MOST/STEPI, POSTECH/BSRI, and Cray R&D (SERI: 97-D2116). K. S. Kim thanks Prof. K. H. Bowen and Prof. M. A. Johnson for helpful discussions. Most calculations were performed with a Cray C90 at SERI.

JA9712377