Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

The dynamic behaviour of a liquid ethanol-water mixture: a perspective from Quantum Chemical Topology

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VIDEO

Ethanol-water-liquid mixture-dynamics-QCT: Dynamic representation (1000 frames) of fluctuating critical points and atomic interaction lines in $(ethanol)_9$-water clusters extracted from a Molecular Dynamics simulation (carried out by the program DLMULTI using a time step of 0.5 fs). The system is in each case rotated to a coordinate frame with the water molecule in the center. The water's geometry is kept fixed, and the rigid-body ethanol molecules move around it. Electron densities are calculated for each frame (snapshot) at the B3LYP/6-31+G(d) level. The pattern of critical points and atomic interaction lines changes with time. The formation and destruction of bond and ring critical points is clearly visible.

Submission of multimedia files

• File name of the video: **Ethanol-water_QCT.avi**

• Short descriptive title for the video that can be used when uploading the video onto a streaming channel: **Ethanol-water-liquid mixture-dynamics-QCT**

• A video legend: **Dynamic representation (1000 frames) of fluctuating critical points and atomic interaction lines in $(ethanol)_9$-water clusters extracted from a Molecular Dynamics simulation.**

• Keywords to tag the video: **quantum chemical topology (QCT), molecular dynamics (MD), bond critical point (BCP) distribution, atoms in molecules, ethanol-water azeotrope, $(ethanol)_9$-water clusters, closed-shell interaction.**

FIGURES

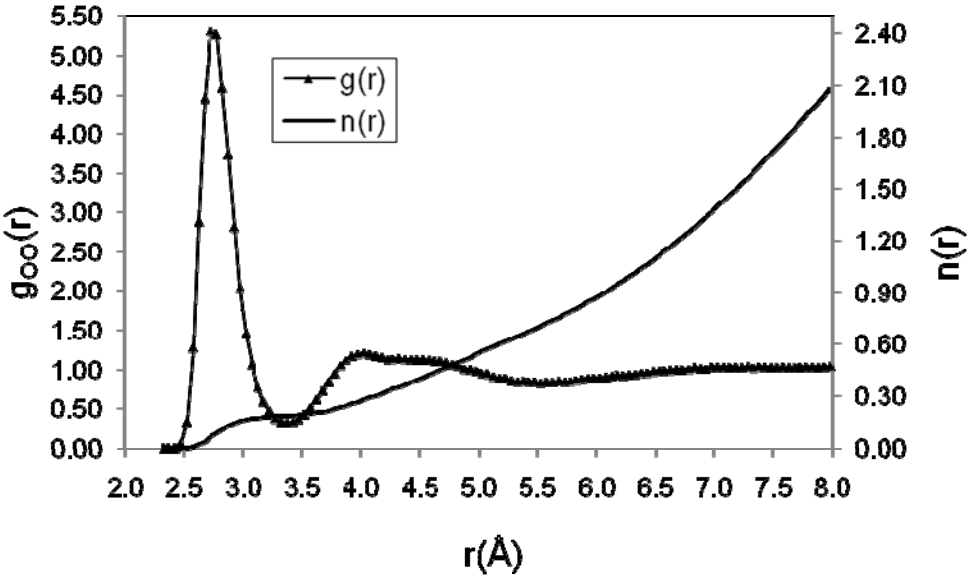

Figure E1. O_{Et}-O_W radial distribution function and integration number n(r) for the ethanol-water mixture.

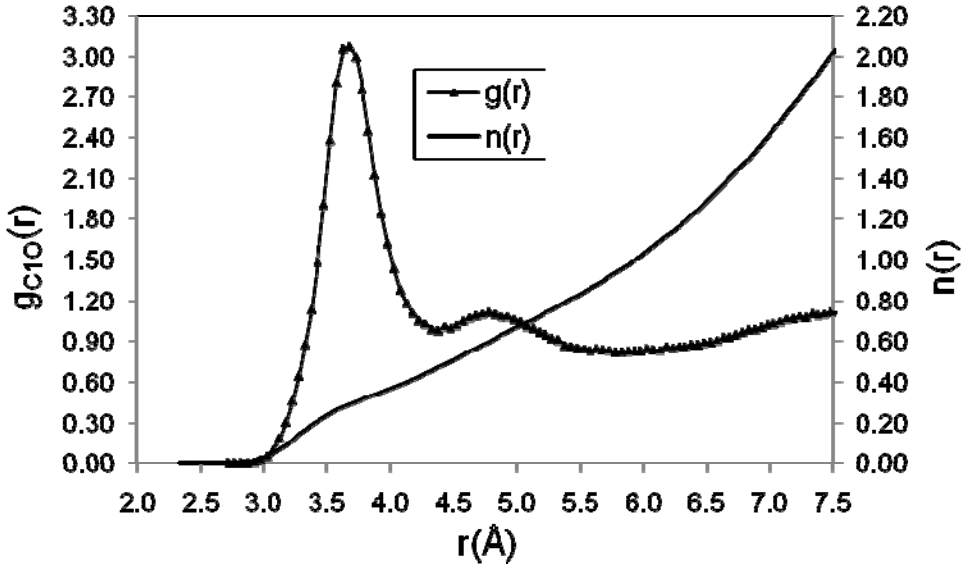

Figure E2. C_1-O_W radial distribution function and integration number n(r) for the ethanol-water mixture. C_1 is the carbon bonded to the hydroxyl group.

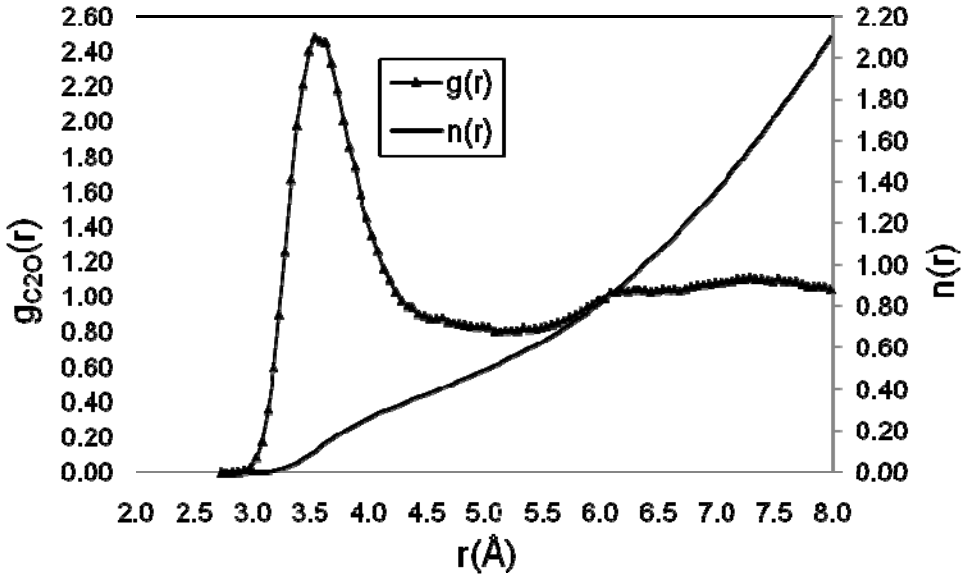

Figure E3. C_2-O_W radial distribution function with integration number n(r) for the ethanol-water mixture. C_2 is the carbon of the methyl group.

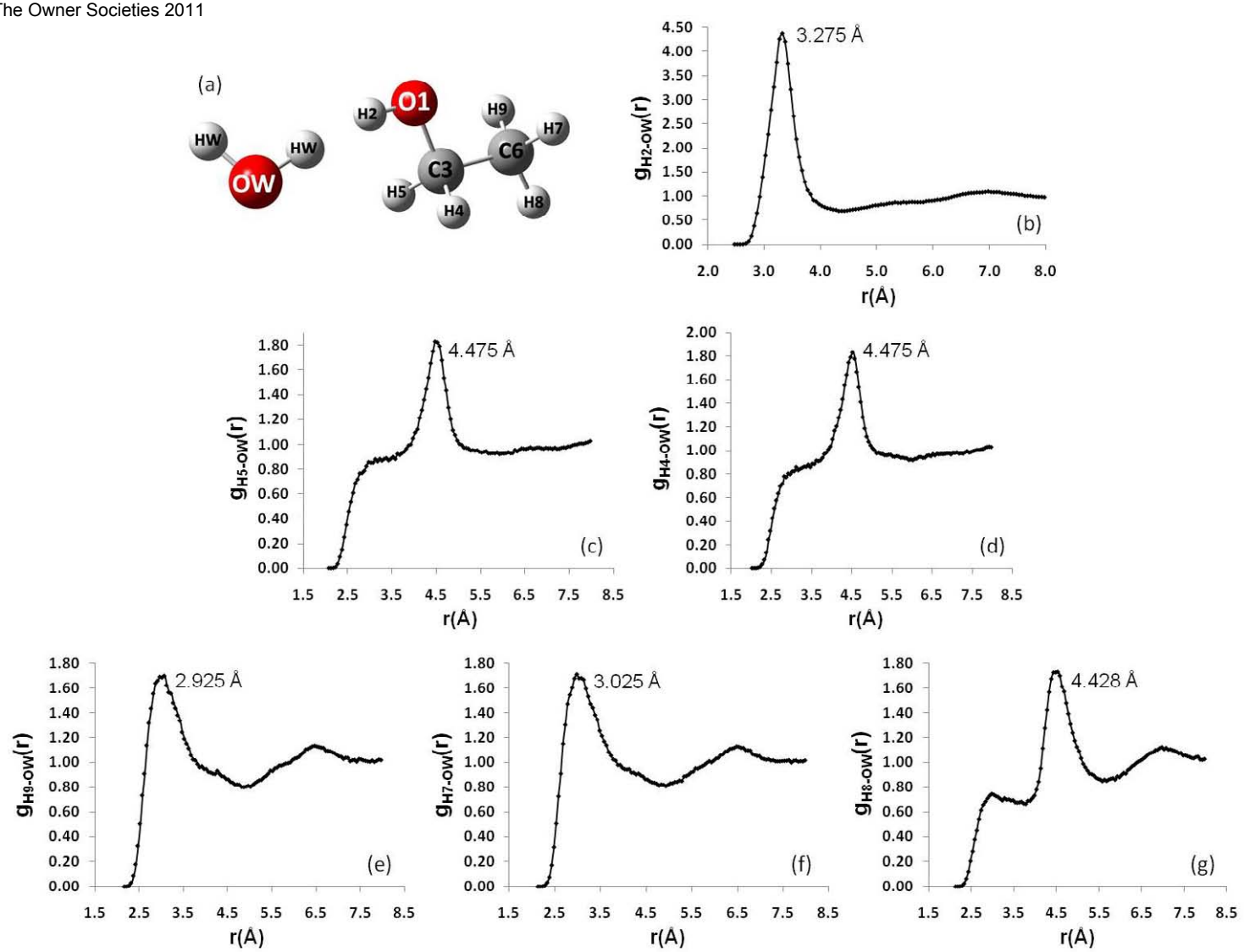

Figure E4. (a) Atomic labels of an isolated water and an isolated ethanol. (b)-(g) Radial distribution functions for the ethanol-water mixture. The distances mark AILs that correspond to (b) O_{Et}-H…O_w hydrogen bonds or (c), (d), (e), (f) and (g) C-H...O_w hydrogen bonds.

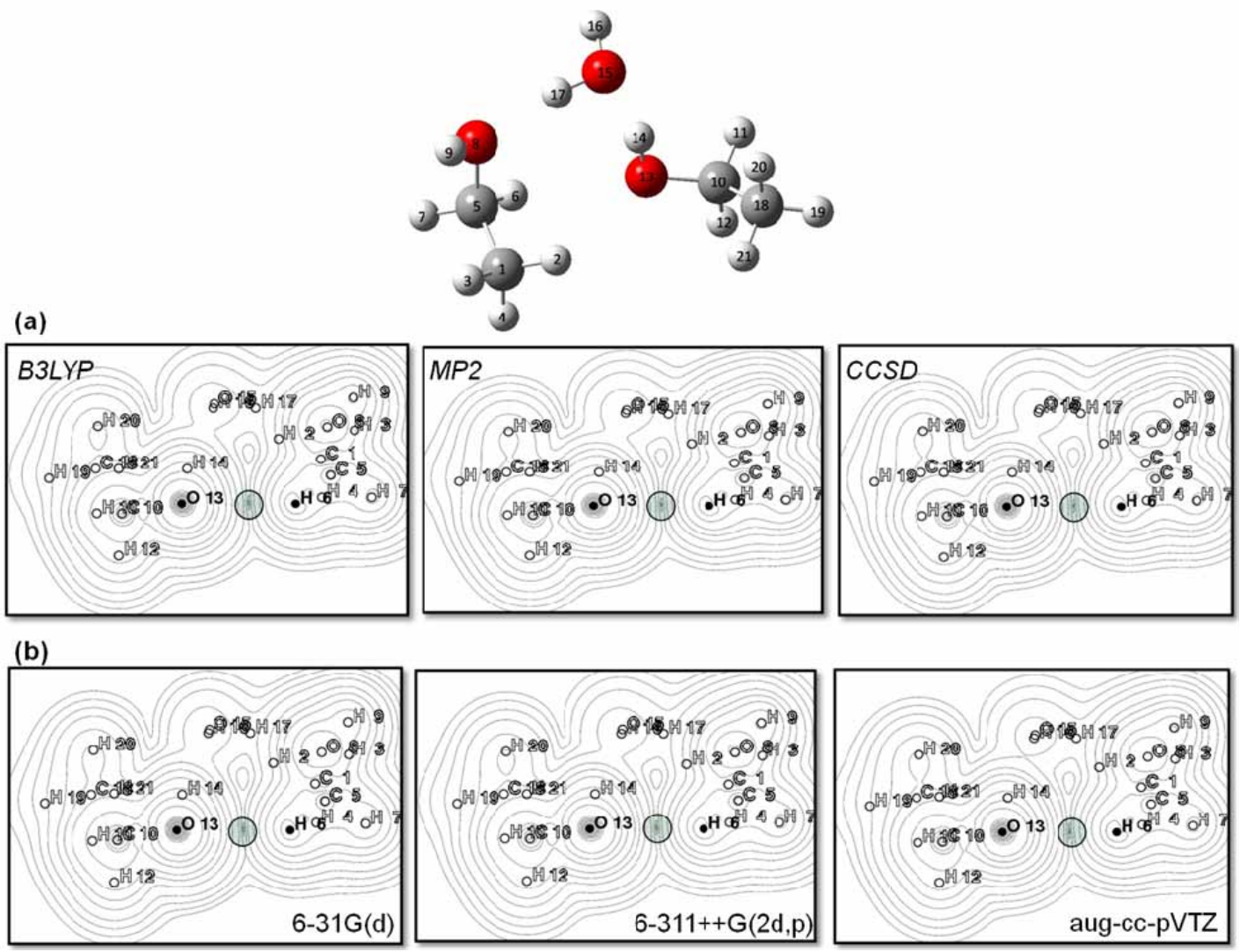

Figure E5. Contour maps of the magnitude of the gradient of the electron density, $|\nabla\rho|$, in the plane formed by atoms H6 and O13, and the corresponding bond critical point. (a) The basis set used for all contour maps is 6-311++G(2d,p) and the methods (B3LYP, MP2, CCSD) are marked in the insets. (b) The method used for all contour maps is B3LYP, and the basis sets are marked in the insets. Light green disks highlight the position of the bond critical point of interest. All atomic labels of the $(ethanol)_2$-water heterotrimer are given below.

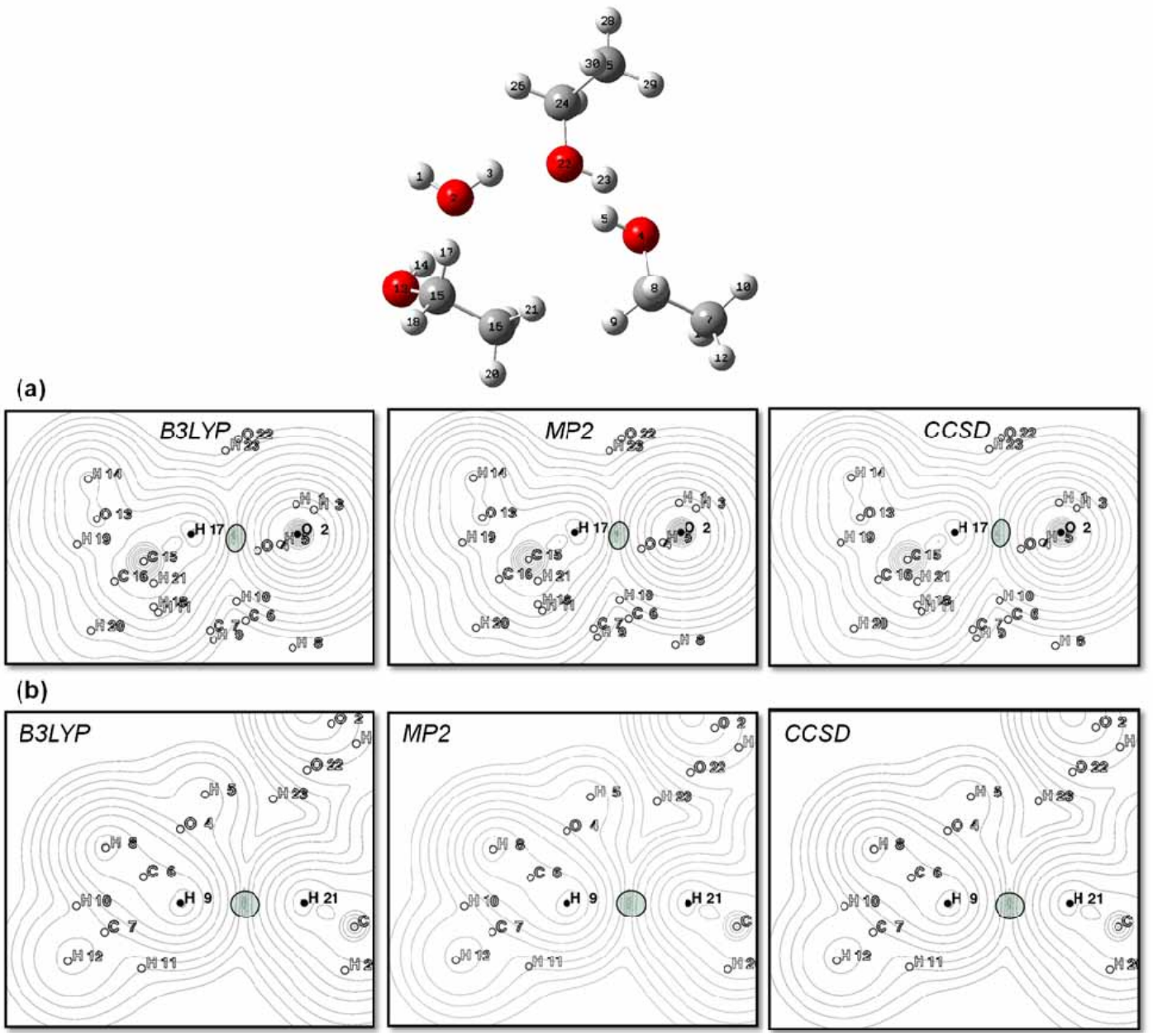

Figure E6. Contour maps of the magnitude of the gradient of the electron density, $|\nabla\rho|$, calculated with the 6-31+G(d) basis set and using three different methods (B3LYP, MP2, CCSD). (a) Maps are shown in the plane formed by atoms O2 and H17, and the corresponding bond critical point position. (b) Maps are shown in the plane formed by atoms H21 and H9, and the corresponding bond critical point position. Light green disks highlight the bond critical point position of interest. All atomic labels of the $(ethanol)_3$-water heterotetramer are given just below.

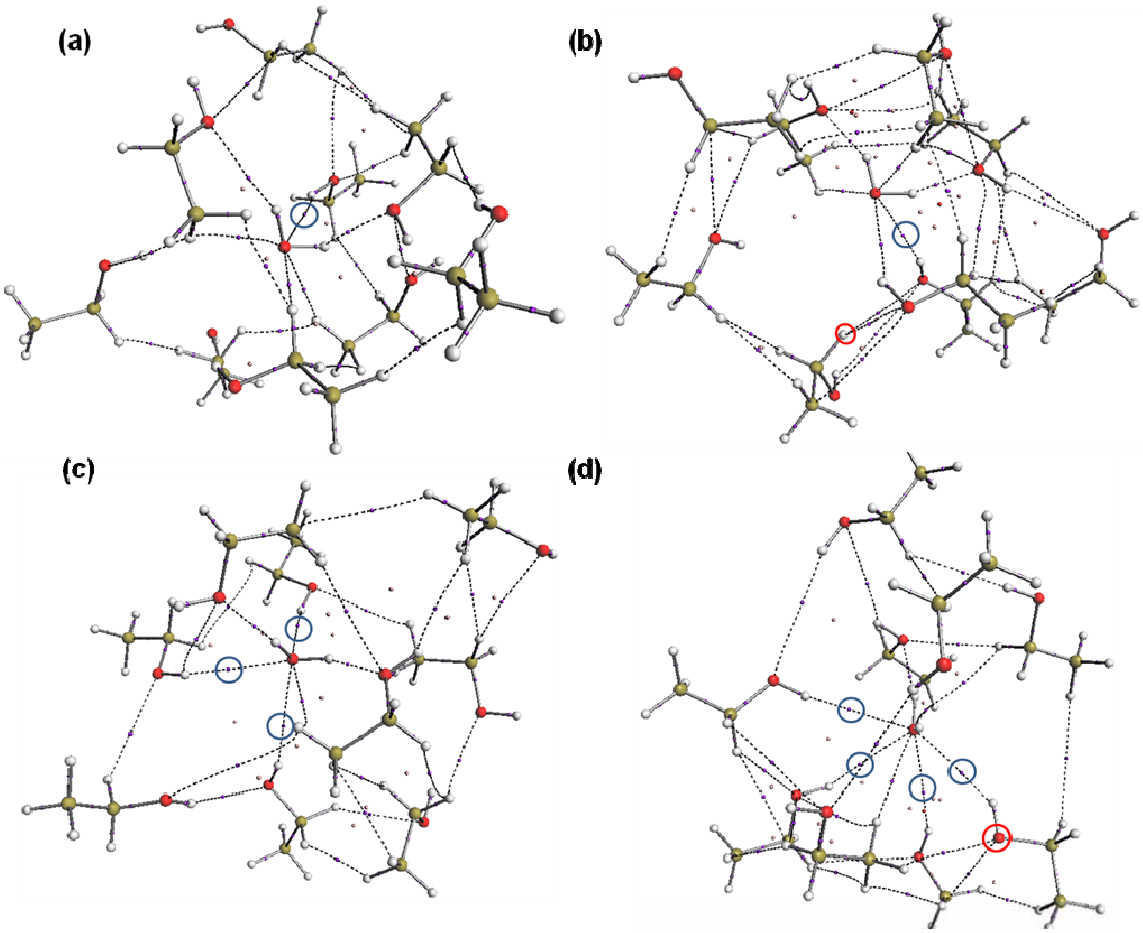

Figure E7. Graphs of atomic interaction lines of four (ethanol)$_9$-water clusters with (a) one, (b) two, (c) three or (d) four O_{Et} -H...O_w interactions (with the water molecule as proton acceptor). The bond critical points for those interactions are marked by blue circles. Examples of atoms involved in bifurcated hydrogen bonds are marked by red circles.

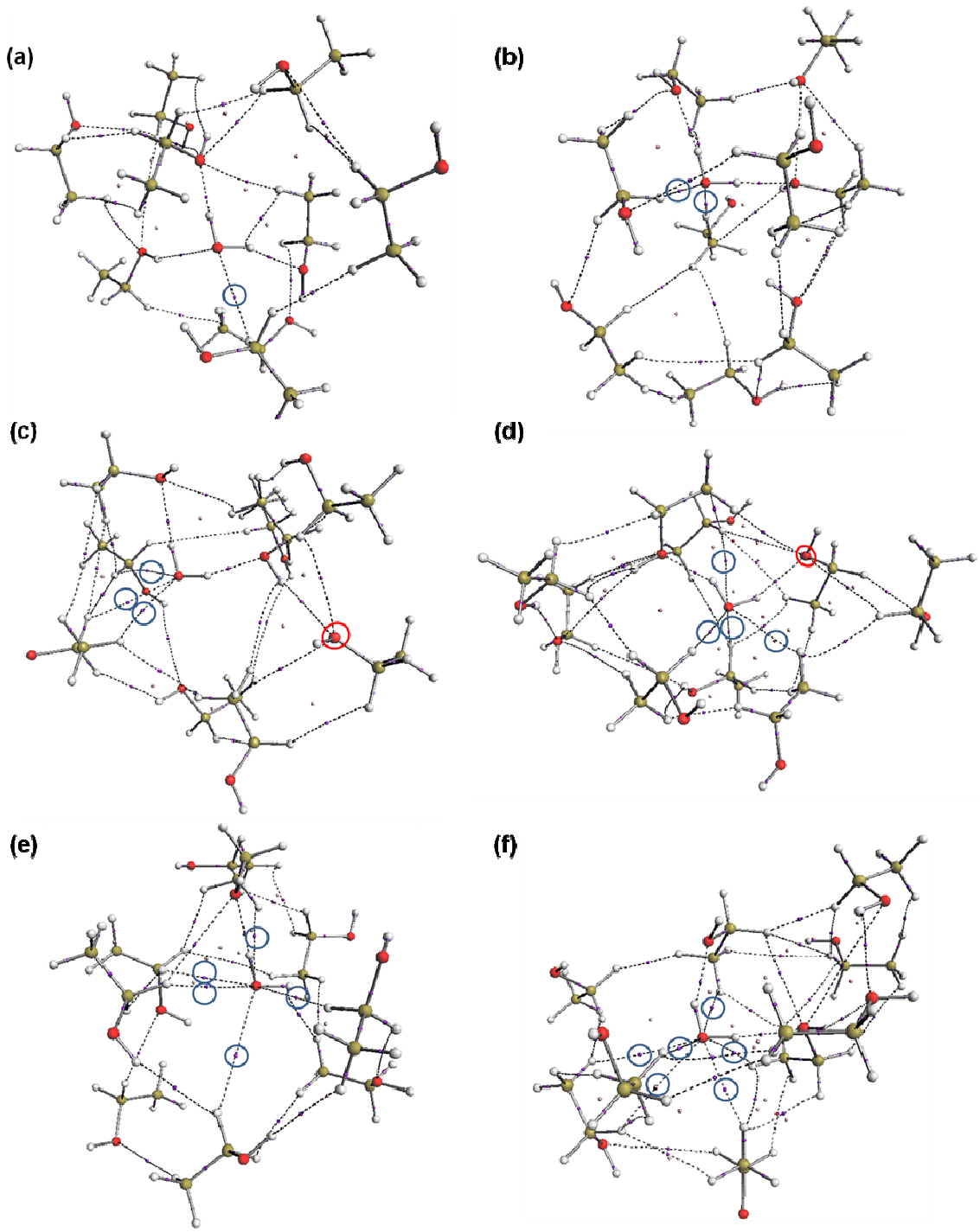

Figure E8. Graphs of atomic interaction lines of six (ethanol)$_9$-water clusters with (a) one, (b) two, (c) three, (d) four, (e) five or (f) six C-H...O$_w$ interactions (with the water molecule as proton acceptor). The bond critical points for those interactions are marked. Examples of atoms involved in bifurcated hydrogen bonds are marked by red circles.

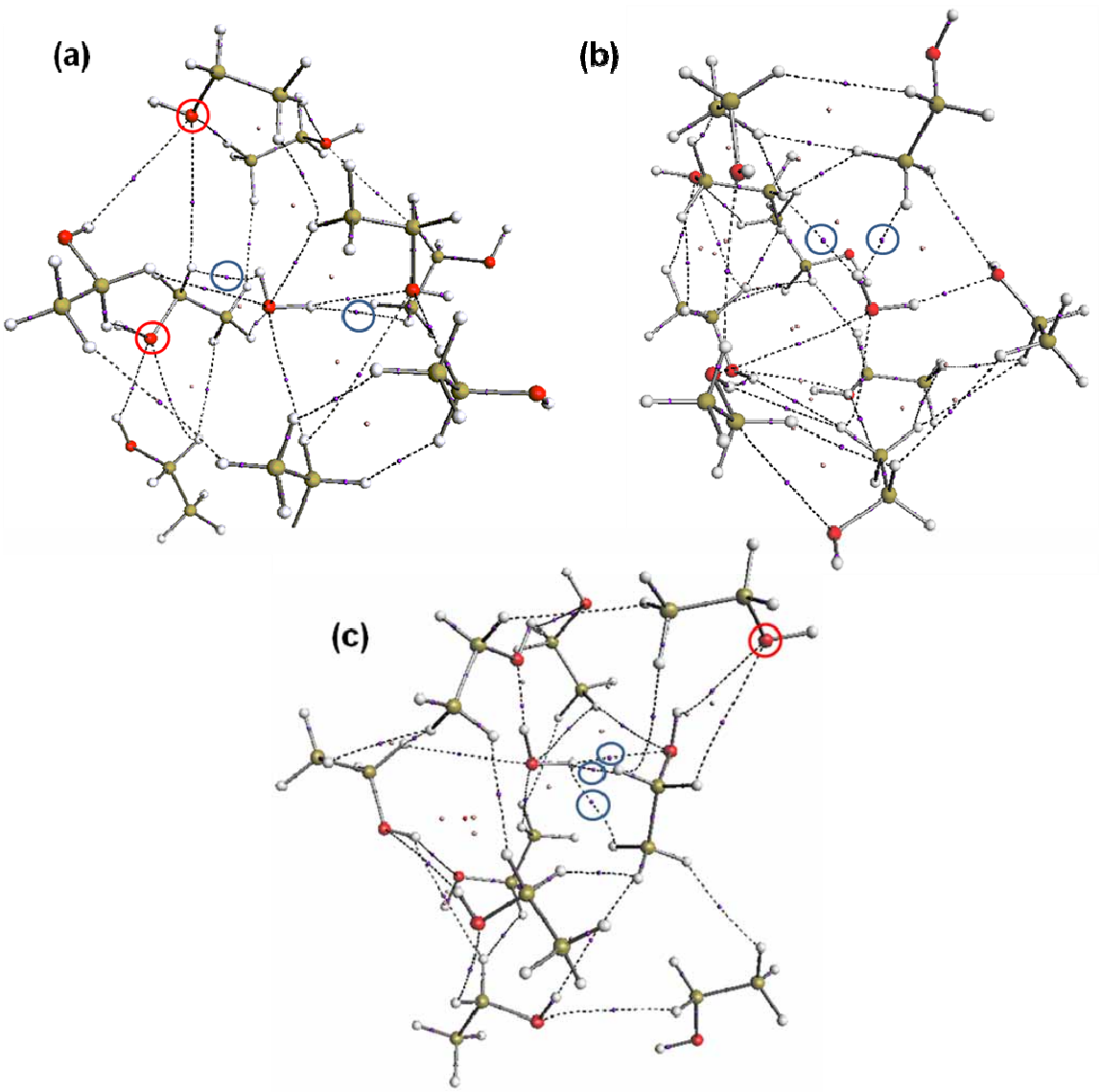

Figure E9. Graphs of atomic interaction lines of three (ethanol)$_9$-water clusters with H...H interactions whose BCPs correspond to the blue points in the BCP distribution of Figure 4 (in the main text). (a) Each water hydrogen atom is involved in one H...H interaction, (b) one water hydrogen is involved in two H...H interactions but that hydrogen is not involved in an O-H...O interaction, (c) one water hydrogen is forming two H...H interactions and one O-H...O hydrogen bond. The bond critical points for those interactions are marked.

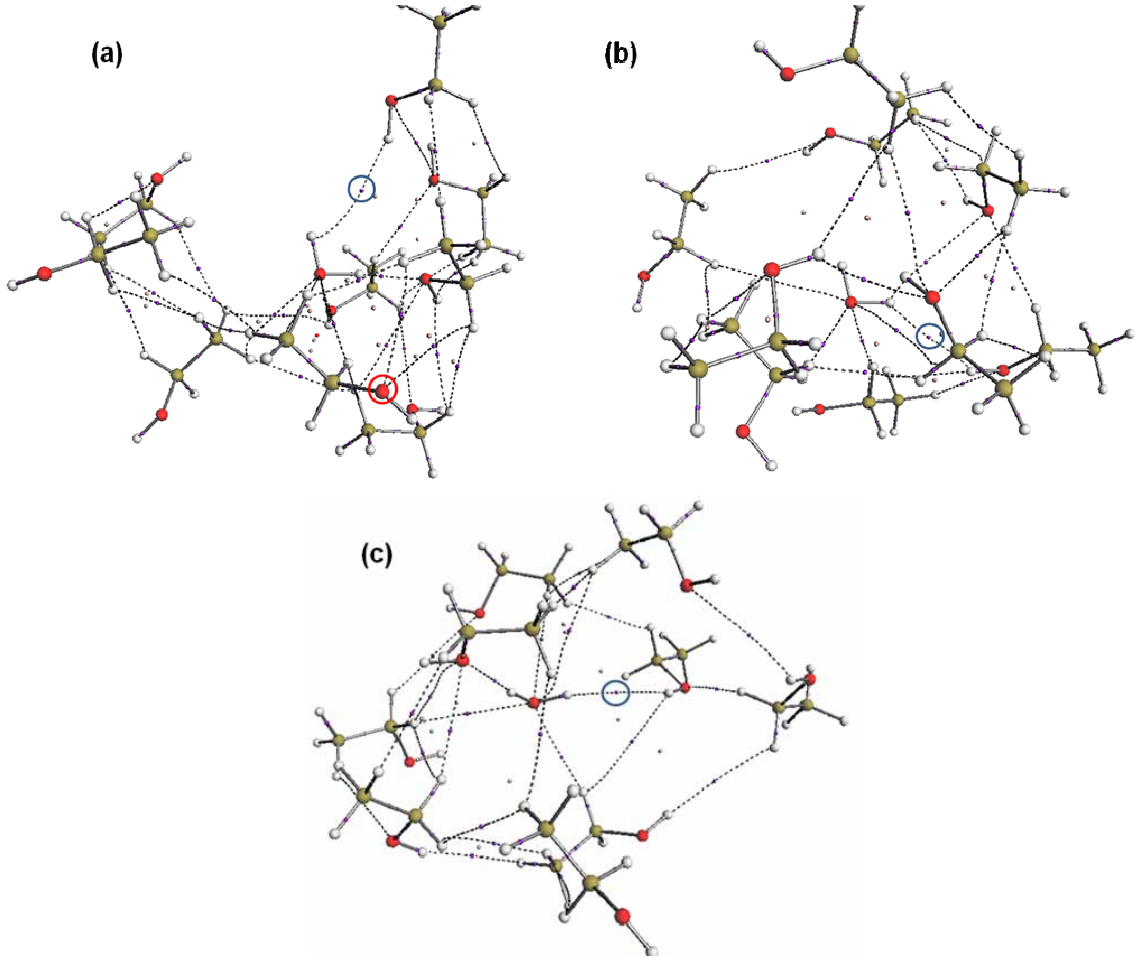

Figure E10. Graphs of atomic interaction lines of three (ethanol)$_9$-water clusters with H...H interactions whose BCPs correspond to the three yellow points enclosed by black circles in the BCP distribution of Figure 4 (in the main text). The BCPs for those interactions are marked.