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Cooperative role of Halogen and Hydrogen Bonding In The Stabilization Of Water Adducts With Apolar Molecules

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Electronic supporting information

Atom-bond pairwise additive representation of the potential energy surface

A realistic description of the potential energy anisotropy is obtained with a formulation that indirectly accounts for the electronic charge distribution along the molecular frame. This approach, which exploits the polarizability partition of a polyatomic molecule in bond tensor components, provides a realistic picture of both the repulsion and the attractive components of a vdW interaction and, in addition, effectively includes both three-body and other nonadditive effects.[1] Accordingly, in this study the interaction centers (a, b) have been localized on the O_2 and D_2O “pseudo” atom and on each of the four C−X bonds of the CX_4 molecule. Therefore, the vdW intermolecular potential component (V_{vdW}) has been taken as a sum of four pseudoatom−bond interaction terms, $V_{vdW} = \Sigma_{ab} V_{ab}$, each one represented by an improved Lennard-Jones (ILJ) function[2] of the type:

$$V_{a,b}(r,\alpha) \;=\; \varepsilon(\alpha)\cdot\left[\frac{6}{n(r,\alpha)-6}\cdot\left(\frac{r_m(\alpha)}{r}\right)^{n(r,\alpha)} - \frac{n(r,\alpha)}{n(r,\alpha)-6}\cdot\left(\frac{r_m(\alpha)}{r}\right)^{6}\right] \qquad (1)$$

where r is the distance of the “pseudo” atom (localized on the O_2 / D_2O CM) from the interaction centre on each bond, and α is the angle that r forms with the axis of the considered bond. Such a simple formulation provides a realistic picture of both the pair repulsion (represented by the first term) and the pair attraction (given by the second term), leading to a proper description of both equilibrium and nonequilibrium geometries of the weakly bound aggregates.[1] The parameter n, which defines the ”fall off” of the atom−bond repulsion, depends on β (related to the hardness of the partners)[2] and is expressed as a function of both r and α using the equation:

$$n(r,\alpha) = \beta + 4\cdot\left(\frac{r}{r_m(\alpha)}\right)^2 \qquad (2)$$

The other potential parameters, i.e., ε and r_m (representing, respectively, the well depth and the equilibrium distance of the relevant interaction pair), depend on the atom−bond orientation angle α, according to assumed functional forms: [2]

$$\epsilon(\alpha) = \varepsilon_{\perp} sin^2(\alpha) + \varepsilon_{\parallel} cos^2(\alpha) \quad (3)$$

$$r_m(\alpha) = r_{m\perp} sin^2(\alpha) + r_{m\parallel} cos^2(\alpha) \quad (4)$$

where ⊥ and ∥ refer, respectively, to the perpendicular and parallel approach of the "pseudo" atom-O_2 / D_2O to the bond. Note that for each interacting pair the asymptotic long-range attraction coefficient is equal to $\varepsilon(\alpha)$ $r_m(\alpha)^6$ and the global attraction coefficient depends on the sum of such components.

As previously,[3-6] in the present investigation each interaction centre on the polyatomic molecules has been localized for C−F and C−Cl bonds at about 60% and 80%, respectively, of the bond length toward the halogen atom.[3, 4] The values of all the ε and r_m potential parameters, reported in the text, have been estimated preliminarily on the basis of the bond polarizability tensor components, which are related to the dimension of the electronic charge distribution around each bond[7] and are consistent with the values of the molecular polarizability.[8] Such components have been combined with the spherical polarizability of O_2 and water (1.6 and 1.47 Å^3, respectively) in the correlation formulas predicting the V_{vdW} parameters (see Refs. [1, 2] and references therein). In obtaining the potential parameters values, it has been also required that at long-range they must generate a global average attraction in substantial agreement with the calculation using the dispersion coefficient ($C_6 = 2.00 \times 10^4$, 1.74×10^4 kJ/mol·Å^6 for O_2- and D_2O-CCl_4, respectively) reported by Kumar.[9] As for Ng−CCl_4,[3, 4, 10, 11] the $r_{m\parallel}$ values have been decreased by about 4% to account of the "polar flattening" effect, due to the anisotropic distribution of the electronic charge around the bound Cl halogen atom, and $\varepsilon_{\parallel}$ adjusted as consequence. The dynamical treatment used for the data analysis (see text) has permitted the satisfactory reproduction of measured cross sections for O_2−CF_4 simply adopting the atom− bond representation of V_{vdW}. However, although the correct "polar flattening" parameters were used, the same methodology was unable to reproduce the experimental data measured for the D_2O-CCl_4 system.

As stressed in the text, the reproduction of the glory pattern, observed for the D_2O-CCl_4 system, has been obtained by introducing a further modification in the potential formulation, concerning the addition of an other stabilizing component, emerging at intermediate and short distance. A contribution associated with possible charge-transfer effects has been included in the potential by adding the term:

$$V_{CT} = -A cos^4(\alpha) e^{-\gamma r} \quad (5)$$

The value of the exponent γ, which defines the "fall off" of the V_{CT} with r, has been assumed to be the same adopted for Ng–CCl_4.[3, 5] Therefore, during the best fit of cross section data, only the pre-exponential A factor has been adjusted; the final value is given in the text (Table 1).

References

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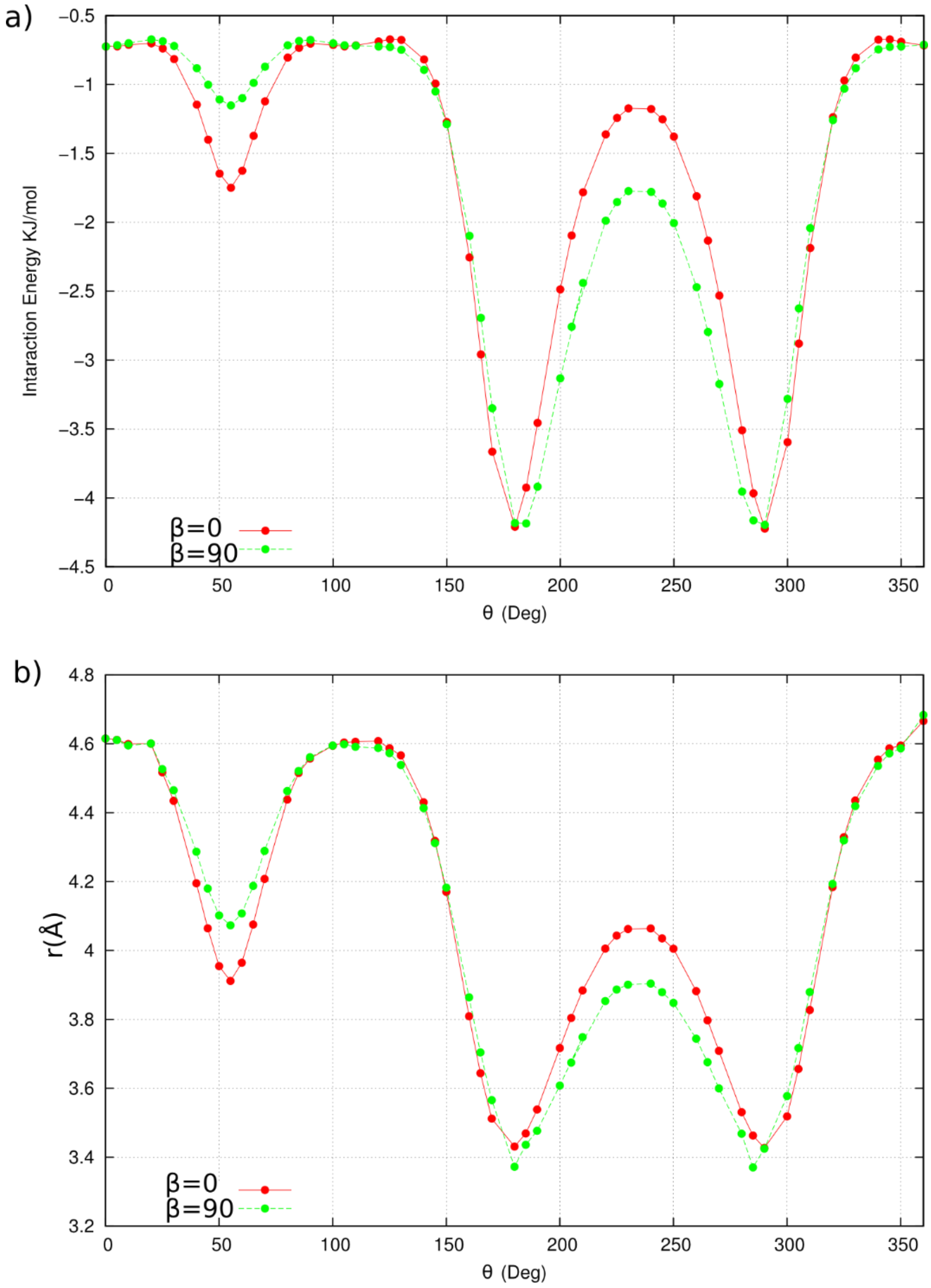

Figure S1. MP2/aug-cc-pVTZ interaction energies (a) and equilibrium distances r_e (b) as a function of the orientation angle θ for the CF_4-water aggregate. Arrangements with oxygen atom of water pointing towards CF_4 and H atoms coplanar (α=0° and γ=0°) and perpendicular (α=0° and γ=90°) are reported in red and green colors, respectively.

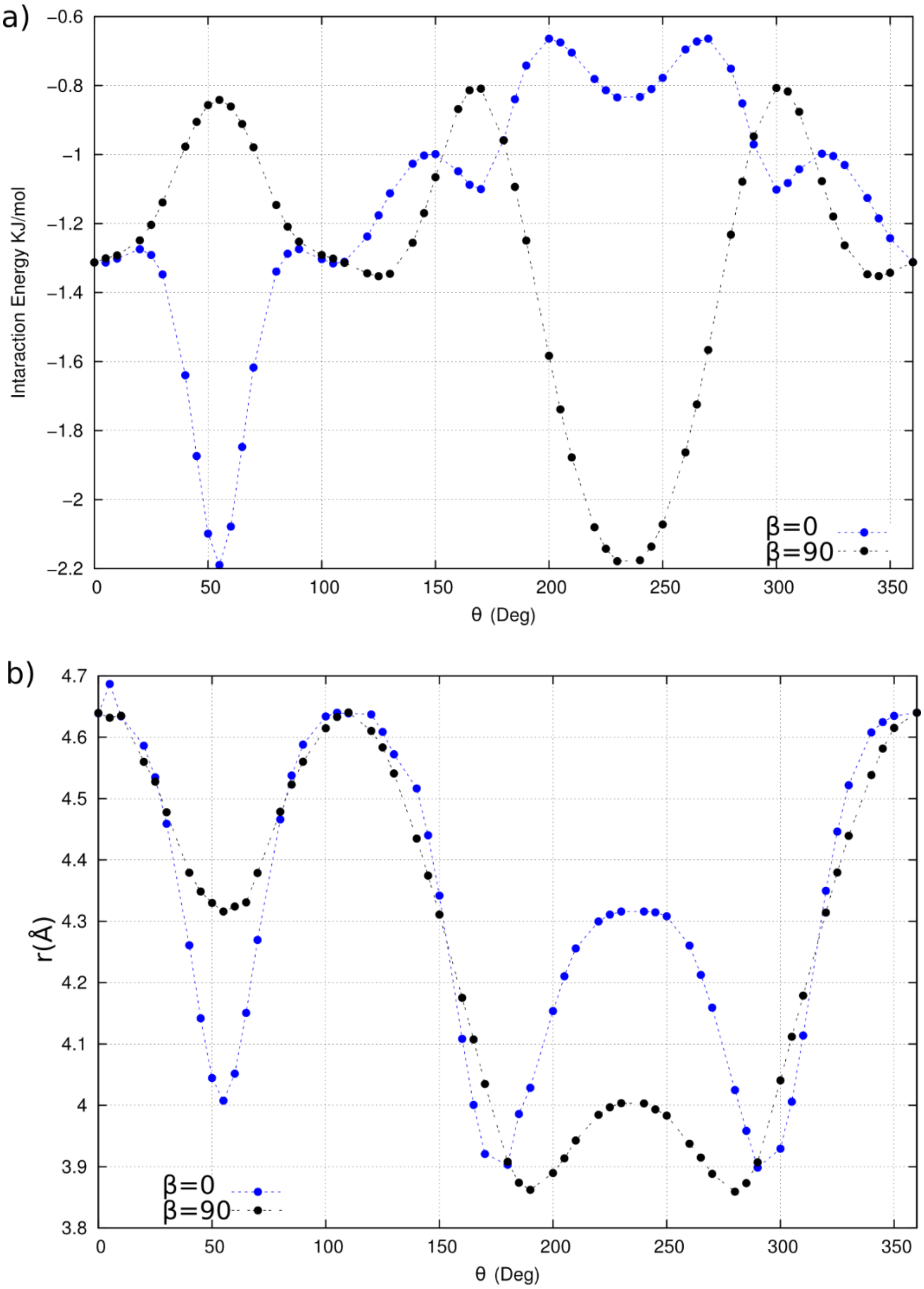

Figure S2. MP2/aug-cc-pVTZ interaction energies (a) and equilibrium distances r_e (b) as a function of the orientation angle θ for the aggregate computed at the MP2/aug-cc-pVTZ level of theory. Arrangements with hydrogen atoms of water pointing towards CF_4 and H atoms coplanar (α=180° and γ=0°) and perpendicular (α=180° and γ=90°) are reported in blue and black colors, respectively.

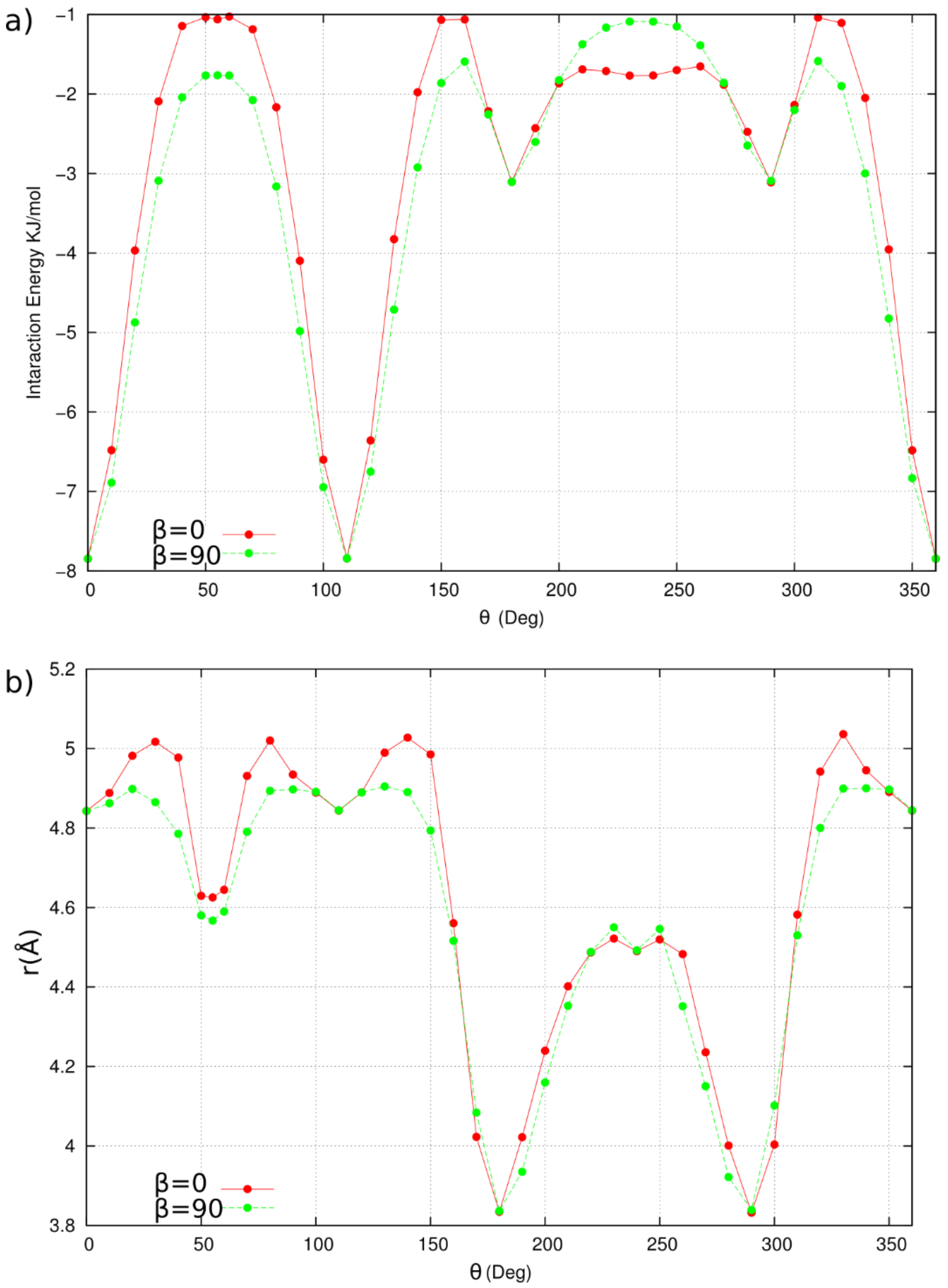

Figure S3. MP2/aug-cc-pVTZ interaction energies (a) and equilibrium distances r_e (b) as a function of the orientation angle θ for the CCl_4-water aggregate. Oxygen atom coplanar (α=0° and γ=0°) and perpendicular (α=0° and γ=90°) arrangements are reported in red and green colors, respectively.

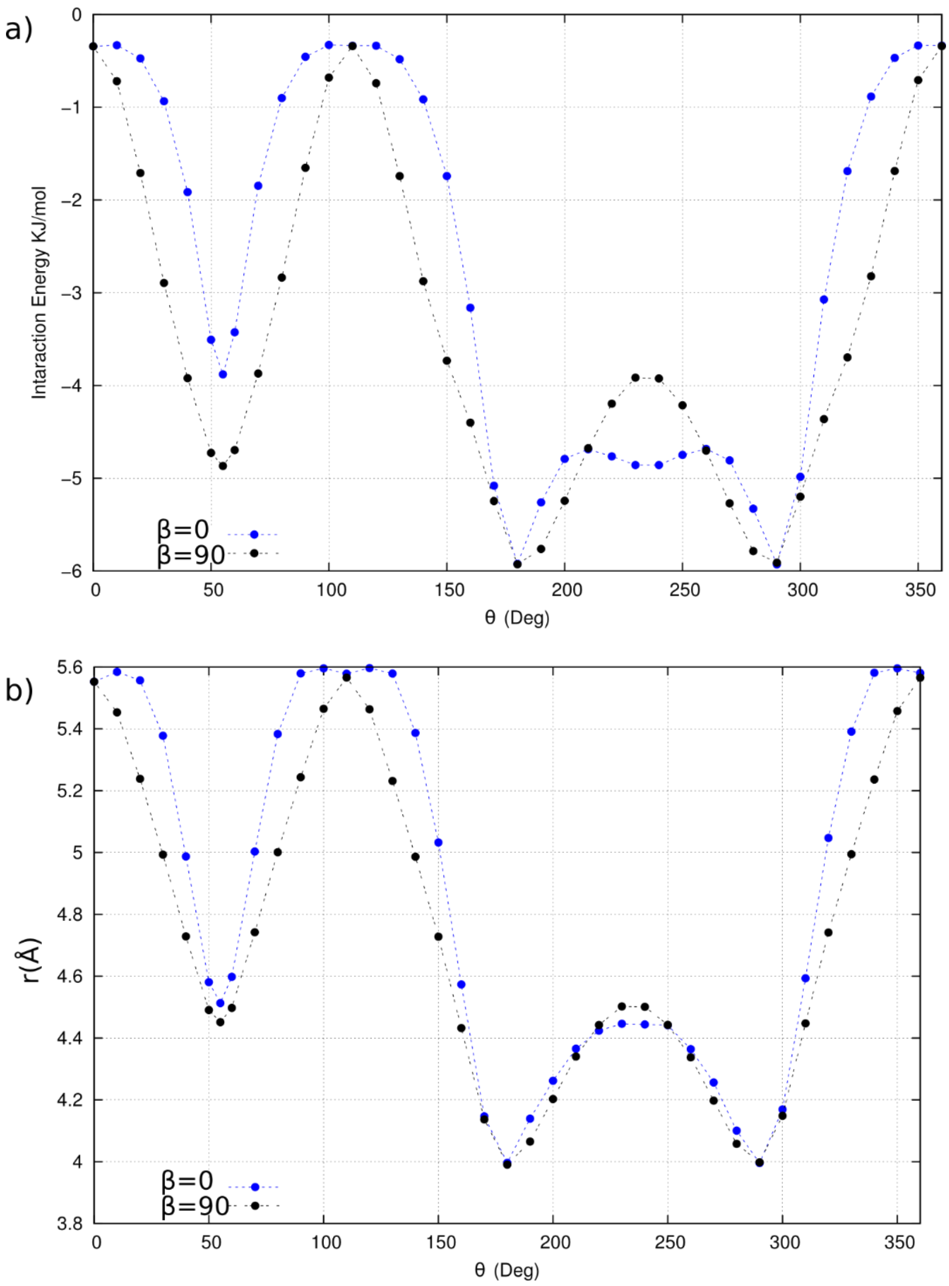

Figure S4. MP2/aug-cc-pVTZ interaction energies (a) and equilibrium distances r_e (b) as a function of the orientation angle θ for the CCl_4-water aggregate computed at the MP2/aug-cc-pVTZ level of theory. Hydrogen atoms coplanar (α=180° and γ=0°) and perpendicular (α=180° and γ=90°) arrangements are reported in blue and black colors, respectively.

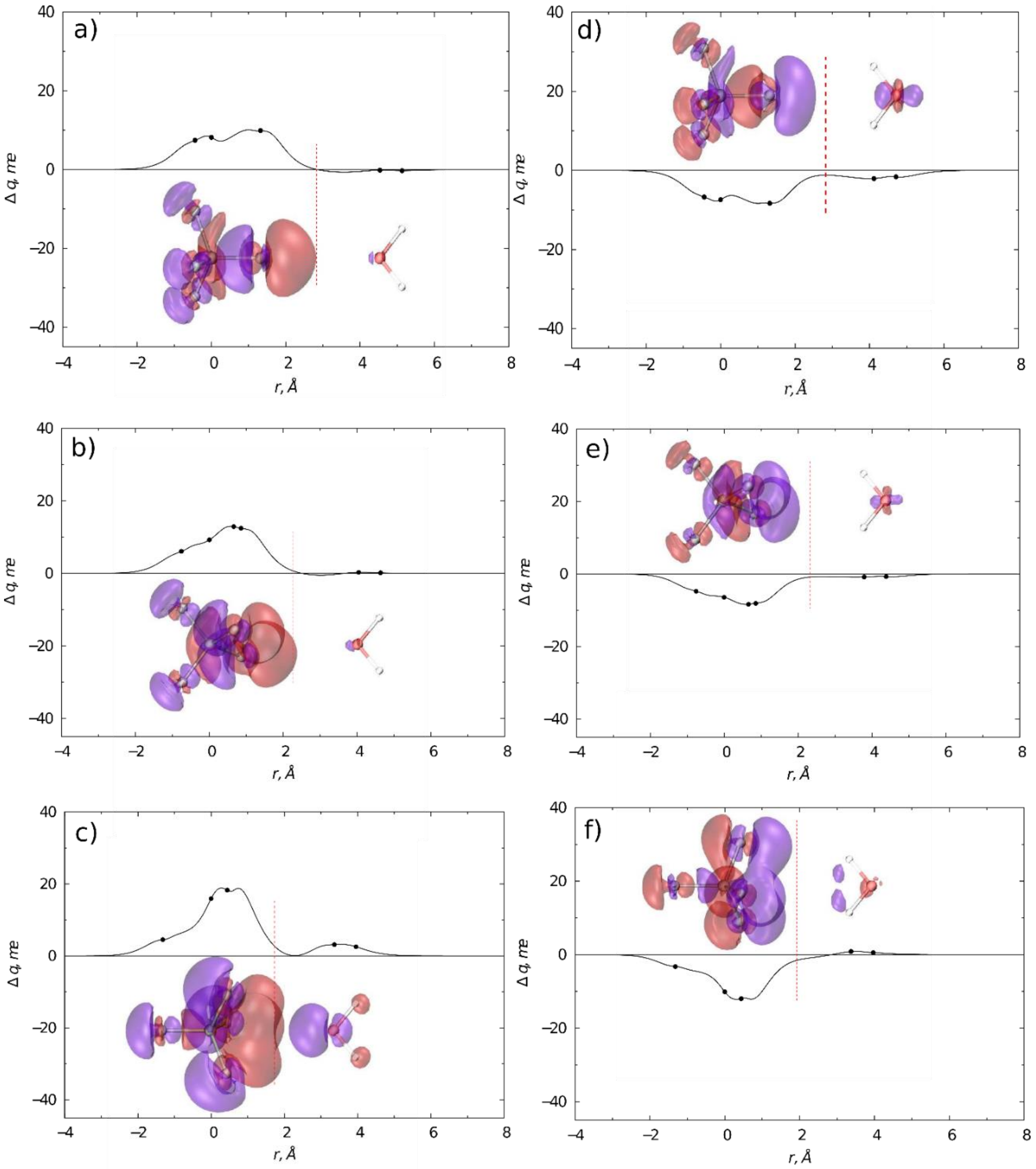

Figure S5. 3D isodensity plots and correspondent CD curves of the electron density change due to the intermolecular interaction for the CF_4-H_2O system with a) $\alpha=0°$, $\theta=0°$, $\gamma=0°$; b) $\alpha=0°$, $\theta=55°$, $\gamma=0°$; c) $\alpha=0°$, $\theta=180°$, $\gamma=0°$; d) $\alpha=180°$, $\theta=0°$, $\gamma=0°$; e) $\alpha=180°$, $\theta=55°$, $\gamma=0°$; f) $\alpha=180°$, $\theta=180°$, $\gamma=0°$. The isodensity surfaces are for $\Delta\rho = \pm 0.15$ me/bohr^3 (negative values in red, positive in violet). The dots correspond to the projection of the nuclei positions on the *z* axis, which is here the axis joining a C−F bond with the H_2O CM. The axis origin is at the tetrahedral carbon. The vertical dashed lines mark the isodensity boundaries between the fragments.

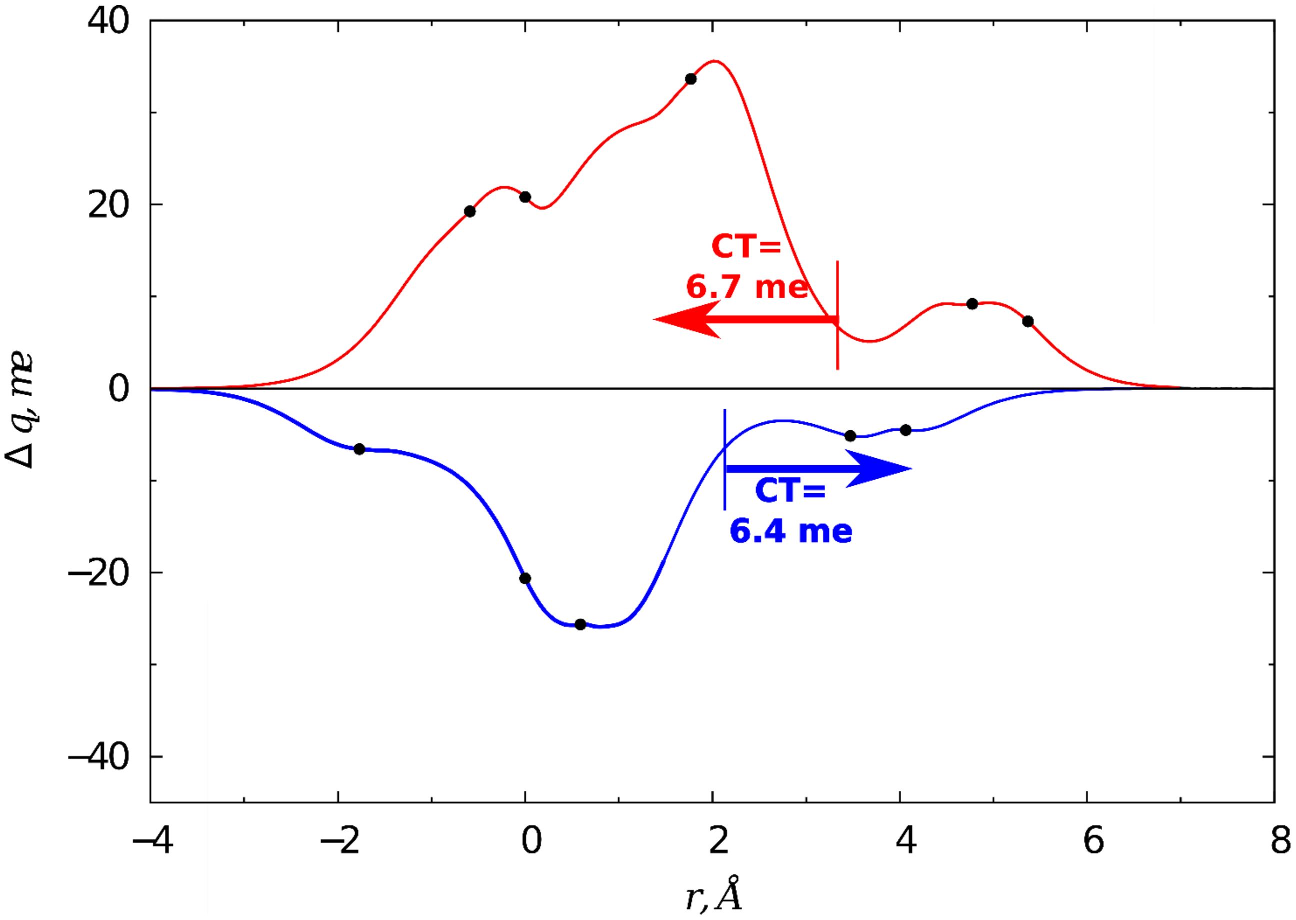

Figure S6. CD curves for the CCl_4-H_2O system with O atom pointing at CCl_4 (dashed line, θ=0°) and with H atoms pointing at CCl_4 (solid line, θ=180°). The dots correspond to the projection of the nuclei positions on the *z* axis, which is here the axis joining a C−Cl bond with the H_2O CM. The axis origin is at the tetrahedral carbon. The vertical lines mark the isodensity boundaries between the fragments.

Full optimized coordinates for the global minimum structure of CF_4-H_2O:

C	-0.0042460026	0.0000029429	0.5709596653
F	0.1497994405	-0.0003904580	1.8898758203
F	-0.6681794140	1.0826094307	0.2110767446
F	1.1908951239	-0.0026628386	-0.0009871838
F	-0.6730443744	-1.0795795111	0.2110132063
O	-0.0276667396	0.0001746765	-2.7594040139
H	-0.4203459839	-0.0017112818	-3.6374755424
H	0.9200824570	-0.0006558636	-2.9243143331

Full optimized coordinates for the global minimum structure of CCl_4-H_2O:

C	0.0000292331	-0.0000012597	-0.4993650067
Cl	-0.0078225643	0.0002754455	1.2649318899
Cl	-0.8341839536	1.4459131400	-1.1030727234
Cl	1.6734473892	0.0014730277	-1.0915649272
Cl	-0.8314591519	-1.4476975803	-1.1026013910
O	-0.0016913053	0.0007644594	4.2663730347
H	-0.7460519105	-0.0053815851	4.8760017626
H	0.7731932614	-0.0054728522	4.8367289713

Full optimized coordinates for the secondary minimum structure of CCl_4-H_2O:

C	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	1.770000
Cl	1.668774	0.000000	-0.589994
Cl	-0.834386	-1.445199	-0.590000
Cl	-0.834386	1.445199	-0.590000
O	-0.067093	-0.116208	-3.697736
H	-0.358012	-0.625560	-4.445016
H	-0.352030	-0.610645	-2.938235