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REGULAR ARTICLE

Magnitude of CH/O interactions between carbohydrate and water

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Abstract The interaction energy potentials for six orientations of the fucose–water complex were calculated for evaluating the magnitude of the CH/O interactions in the complex. The calculations show that the C–H bonds of the nonpolar surface of fucose prefer to have contact with the oxygen atom of the water. The substantial attraction exists between the C–H bonds of fucose and water. The interaction energy calculated for the fucose–water complex at the MP2/aug-cc-pVTZ level is −2.55 kcal/mol. The CH/O interactions in the fucose–water complex are significantly larger than those in the cyclohexane–water complex (−1.13 kcal/mol), which shows that the oxygen atoms of fucose enhance the CH/O interactions. The electrostatic and dispersion interactions are responsible for the attraction in the CH/O interactions in the fucose–water complex, while the electrostatic contributions to the attraction in the CH/O interactions in the cyclohexane–water complex is small. The DFT-SAPT calculations also show that the electrostatic interactions are responsible for the larger attraction in the fucose–water complex. These results suggest that the nature of the CH/O interactions between carbohydrate and water is significantly different from that of the CH/O interactions between saturated hydrocarbon and water.

Keywords CH/O interactions · Ab initio calculations · Weak intermolecular interactions · Carbohydrate–water interactions · Electrostatic interactions · Dispersion interactions · DFT-SAPT calculation

1 Introduction

Protein–carbohydrate interactions play important roles in a broad range of biological processes [1–3]. A variety of proteins are involved in carbohydrate recognition, including enzymes, antibodies and lectins [3, 4]. The elucidation of the mechanisms that control carbohydrates recognition in binding sites of the receptor proteins is currently a central issue of major interest. NMR and X-ray diffraction data show that the protein–carbohydrate recognition is generally established through networks of hydrogen bonds and complementary contact between nonpolar surfaces [5–10]. Polar side chain groups and main chain amides are used for hydrogen bonding. Nonpolar surfaces of carbohydrates often have stacking with aromatic residues. The carbohydrate–aromatic interactions, which are sometimes denoted as CH/π interactions, were used for recognition of carbohydrates by artificial receptors [11–14]. The carbohydrate–aromatic interactions have been studied extensively both by experimental [15–23] and by theoretical [24–35] methods. The carbohydrate recognition processes involve desolvation of water molecules from the carbohydrate molecule. The hydroxyl groups of carbohydrates have hydrogen bonds with surrounding water molecules. Some water molecules have contact with the C–H bonds in the nonpolar surfaces of carbohydrates, which suggests that the

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carbohydrate–water interactions (CH/O interactions) also play important roles in the carbohydrate recognition processes. Therefore, the CH/O interactions of the C–H bonds of carbohydrates with the oxygen atom of water are also important for understanding the mechanism of the carbohydrate recognition processes. A quantitative evaluation of the nature of the CH/O interactions of carbohydrate molecules (magnitude, orientation dependence and origin of attraction) is necessary for understanding their roles in the molecular recognition processes.

The CH/O interactions of small hydrocarbon molecules have been studies extensively both by experimental [36–59] and by theoretical [60–73] methods. A few experimental studies on the CH/O interactions of carbohydrate molecules were reported [55–59], in which the CH/O interactions were studied by crystal structure analysis and by spectroscopic measurements. Unfortunately, however, a quantitative evaluation of the CH/O interactions of carbohydrate molecules was not reported. The details of the CH/O interactions of carbohydrates are still unclear. Recently reported ab initio calculations of small clusters show that the calculations well reproduce the experimental binding energies of clusters in the gas phase, if a reasonably large basis set is used and electron correlation is corrected properly [74–76]. In this paper, we studied the CH/O interactions between the fucose and water by high-level ab initio calculations. We calculated the MP2 level interaction energy at the basis set limit for analyzing the magnitude of interaction energy and its orientation dependence. We discussed the effects of oxygen atoms of fucose on the magnitude of the CH/O interactions by comparing with the CH/O interactions in the cyclohexane–water, methane–water, propane–water and dimethylether–water complexes.

2 Computational method

The Gaussian 03 program [77] was used for the ab initio molecular orbital calculations. Electron correlation was accounted for by the second-order Mϕller-Plesset perturbation (MP2) method [78, 79] and by coupled cluster calculations with single and double substitutions with noniterative triple excitations [CCSD(T)] [80]. The basis set superposition error (BSSE) [81] was corrected for all calculations using the counterpoise method [82]. The geometries for an isolated fucose and a water were optimized at the MP2/6-311G** level. The optimized geometries were used for calculating the interaction energy potentials without further geometry optimization. The most stable conformation of fucose [30] was used. The MP2 level interaction energy at the basis set limit [$E_{MP2(limit)}$] for the complex was obtained by Helgaker's method [83] from the MP2 interaction energies (E_{MP2}) obtained using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The electrostatic energy was calculated as the interactions between distributed multipoles [84, 85] of interacting molecules using ORIENT version 3.2 [86]. Distributed multipoles up to hexadecapole on all atoms were obtained from the MP2/cc-pVTZ wave functions of isolated molecules using the GDMA program [87]. The induction energy was calculated as the interactions of polarizable sites with the electric field produced by the distributed multipoles of monomers [88]. The atomic polarizabilities of carbon ($\alpha = 10$ au) and oxygen ($\alpha = 6$ au) were used for the calculations [89]. The distributed multipoles were used only to estimate the electrostatic and induction energies. The electrostatic, induction and dispersion energies were also evaluated by DFT-SAPT calculations [90] using the pbe0 functionals [91] and the cc-pVDZ basis set. The DFT-SAPT calculations were carried out using MOLPRO program [92]. The atomic charges of an isolated fucose were obtained by electrostatic potential fitting using the Merz-Singh-Kollman scheme [93, 94] from the MP2/cc-pVTZ level wave functions.

3 Results and discussion

3.1 Effects of basis set

The intermolecular interaction energy for the fucose–water complex (Fig. 1, orientation **A**) was calculated at the MP2 level with several basis sets for evaluating the basis set effects. The intermolecular distance is the distance between the oxygen atom of water and the center of gravity of the three carbon atoms (C_1, C_3 and C_5) of the fucose (**X**). The **X**…O (water oxygen atom) is perpendicular to the plane defined by the three carbon atoms (C_1, C_3 and C_5) in the orientation **A**. The **X**…O is on the C_2 symmetry axis of the water. The C_5 is on the symmetry (H–O–H) plane of the water.

The MP2 level interaction energy potentials calculated for the complex using several basis sets are shown in Fig. 2. The estimated MP2 level interaction energy at the basis set limit [$E_{MP2(limit)}$] is also shown. The $E_{MP2(limit)}$ has a potential minimum when the intermolecular distance is 3.4 Å. The $E_{MP2(limit)}$ calculated at the potential minimum is −2.73 kcal/mol. The potential depth calculated using the aug-cc-pVTZ basis set (−2.55 kcal/mol) is close to that of the $E_{MP2(limit)}$, which shows that the aug-cc-pVTZ basis set is close to saturation.[1] Therefore, we decided to evaluate the orientation dependence of the interaction energy for the

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[1] Similar basis set dependence was reported in the calculations of the fucose–benzene (carbohydrate-aromatic) interactions [30].

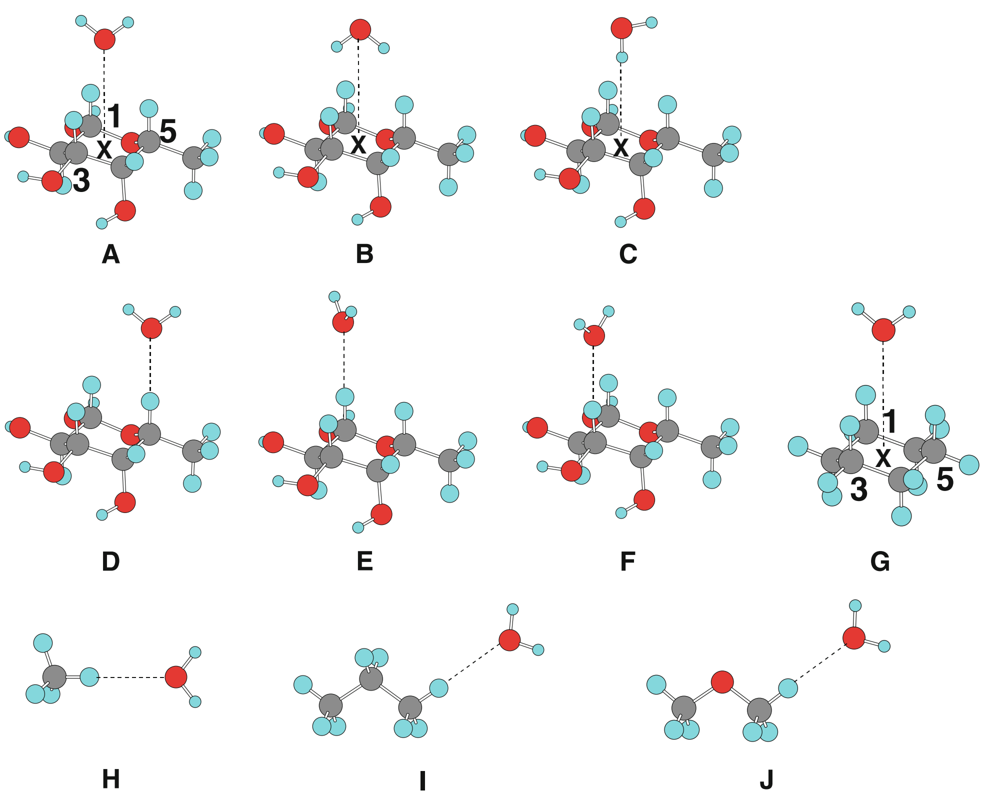

Fig. 1 Geometries of the fucose–water (**A**–**F**), cyclohexane–water (**G**), methane–water (**H**), propane–water (**I**) and dimethylether–water (**J**) complexes

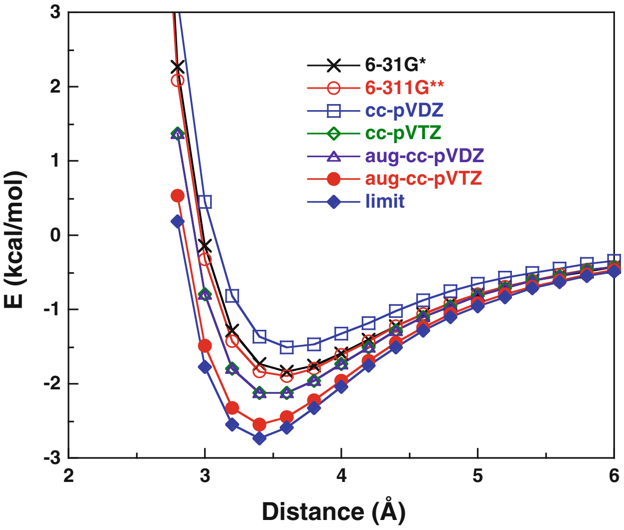

Fig. 2 Basis set effect on interaction energy calculated for the orientation **A** fucose–benzene complex. Electron correlation was corrected by the MP2 method. The estimated MP2 interaction energy at the basis set limit [$E_{MP2(limit)}$] was also shown as (limit). The geometry for the complex is shown in Fig. 1

fucose–water complex using the aug-cc-pVTZ basis set in this work. Small basis sets underestimate the attraction significantly as shown in Fig. 2. The calculated interaction energies using the 6-31G*, 6-311G*, cc-pVDZ, cc-pVTZ and aug-cc-pVDZ basis set at the same intermolecular distance are −1.74, −1.84, −1.36, −2.12, −2.12 kcal/mol, respectively. The strong basis set dependence of the calculated interaction energies was also reported in the calculations of small model clusters for the CH/O interactions [63].

3.2 Effects of electron correlation

The effects of electron correlation beyond MP2 were evaluated. The interaction energy potentials for the orientation **A** fucose–water complex were calculated using several electron correlation correction methods with the 6-31G* basis set as shown in Fig. 3. The effects of electron correlation beyond the MP2 are very small. The MP2, MP3, CCSD and CCSD(T) potentials have potential minima when the intermolecular distance is 3.6 Å. The calculated interaction energies at the potential minima are −1.83, −1.93, −1.83 and −1.81 kcal/mol, respectively. The MP2 level potential is nearly identical to the CCSD(T) level potential. The good performance of the MP2 method was also reported in the calculations of small model clusters for the CH/O interactions [63]. Therefore, we decided to evaluate the magnitude and orientation dependence of the interaction energy in the fucose–water complex using the MP2 method in this work.[2] The HF level

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[2] In contrast the effects of electron correlation beyond MP2 is significant in the fucose–benzene (carbohydrate-aromatic) interactions [30].

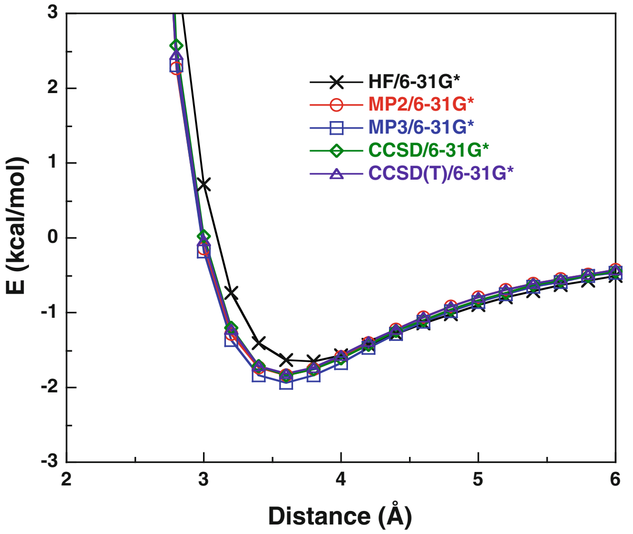

Fig. 3 Electron correlation effects on interaction energy calculated for the orientation **A** fucose–benzene complex. The 6-31G* basis set was used. The geometry for the complex is shown in Fig. 1

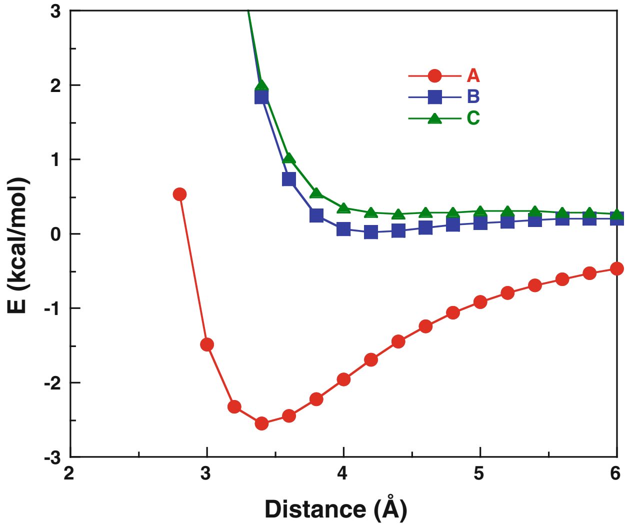

Fig. 4 Interaction energy potentials calculated for three orientations of the fucose–water complex at the MP2/aug-cc-pVTZ level. The geometries for the complex are shown in Fig. 1

potential has a shallower minimum, which shows that the dispersion interactions contribute to the attraction in the fucose–water complex.

3.3 Orientation dependence of interaction energy

The interaction energy potentials calculated for the six orientations of the fucose–water complex (Fig. 1) at the MP2/aug-cc-pVTZ level are compared for evaluating the orientation dependence of the interaction energy. The positions of the water oxygen atom in the orientations **B** and **C** are the same as that in the orientation **A**. The **X**…O is on the C_2 symmetry axis of the water in the orientation **B**. The **X**…O is on an O–H bond of the water in the orientation **C**. The C_5 is on the symmetry plane of the water in the orientations **B** and **C**. The intermolecular distance in the orientations **B** and **C** is the **X**…O distance. One of the C–H bonds in the nonpolar surface of fucose is on the C_2 symmetry axis of the water in the orientations **D**–**F**. The **X** is on the symmetry plane of the water in the orientations **D**–**F**. The intermolecular distance in the orientations **D**–**F** is the distance between the oxygen atom of the water and the carbon atom of the interacting C–H bond.

The interaction energy potential calculated for the orientation **A** (Fig. 4) has substantially deep potential minimum (−2.55 kcal/mol), while the potentials calculated for the orientations **B** and **C** are always repulsive. The calculated potentials for the three orientations **A**–**C** show that the C–H bonds in the nonpolar surface of fucose prefer to have contact with the oxygen atom of the water. The potentials calculated for the three orientations (**D**–**F**) have shallower potential minima compared with the orientation **A** (Fig. 5). The depths of the potentials calculated for the three orientations **D**–**F** are −1.97, −1.64 and −1.62 kcal/mol, respectively. The oxygen atom of water has contact with three C–H bonds in the orientation **A**, while only one C–H bond has contact with the oxygen atom in the orientations **D**–**F**. The interactions with the three C–H bonds will be the origin of the stronger attraction in the orientation **A** compared with that in **D**–**F**.

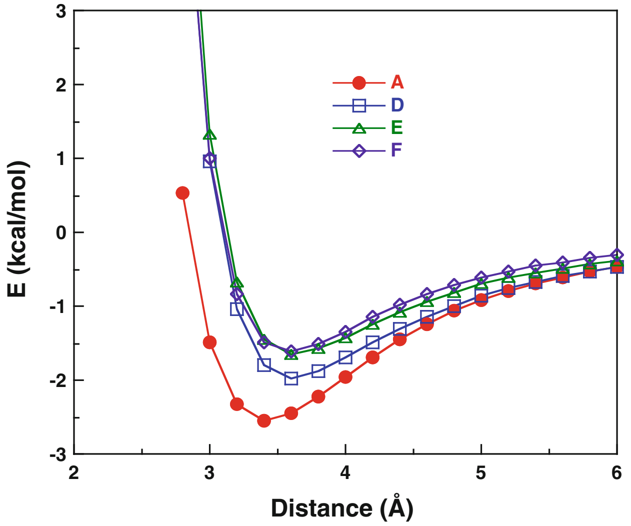

Fig. 5 Interaction energy potentials calculated for four orientations of the fucose–water complex at the MP2/aug-cc-pVTZ level. The geometries for the complex are shown in Fig. 1

3.4 Comparison with cyclohexane–water, methane–water, propane–water and dimethylether–water interactions

The interaction energy potentials for the cyclohexane–water, methane–water, propane–water and dimethylether–water complexes (Fig. 1, **G**–**J**) were calculated at the MP2/aug-cc-pVTZ level for comparing with the CH/O interactions in the fucose–water complex. The intermolecular distance in the cyclohexane–water complex (**G**) is the distance between the oxygen atom of water and the center of gravity of the three carbon atoms (C_1, C_3, and C_5) of the cyclohexane (**X**). The **X**…O (water oxygen atom) is on the C_3 axis of the cyclohexane. The **X**…O is on the C_2 axis of the water. Two carbon atoms of the cyclohexane are on the symmetry plane of the water. The intermolecular distances in other three complexes (**H**–**J**) are the distances between the carbon atom of the interacting C–H bond and the water oxygen atom. The water oxygen atoms are on the C–H bonds in the complexes. The C…O is on the C_2 axis of the water. These complexes have C_s symmetry.

The interaction energy potentials calculated for the four complexes are compared with that calculated for the orientation **A** fucose–water complex as shown in Fig. 6. The depth of the potential calculated for the fucose–water complex **A** (−2.55 kcal/mol) is substantially larger (more negative) than that for the cyclohexane–water complex **G** (−1.13 kcal/mol). Similar change of the potential depth was observed in the calculations of the complexes **H**–**J**. The depth of the potential calculated for the dimethylether–water complex **J** (−0.91 kcal/mol) is substantially larger than those of the potentials calculated for the methane–water and propane–water complexes **H** and **I** (−0.57 and −0.59 kcal/mol, respectively). The calculated potentials for the complexes show that the oxygen atoms attached to the carbon atom of the C–H bonds enhance the CH/O interactions in the fucose–water and dimethylether–water complexes.[3]

3.5 Role of electrostatic, dispersion and charge-transfer interactions

The electrostatic energies (E_{es}), induction energies (E_{ind}) and the electron correlation contributions to the total interaction energies ($E_{corr} = E_{int} - E_{HF}$) for the fucose–water **A** and cyclohexane–water complexes **G** at the potential minima are summarized in Table 1. We discuss the magnitude of the dispersion contribution to the attraction based on the size of E_{corr}.[4] The E_{rep} (=$E_{HF} - E_{es} - E_{ind}$) is mainly exchange-repulsion energy.

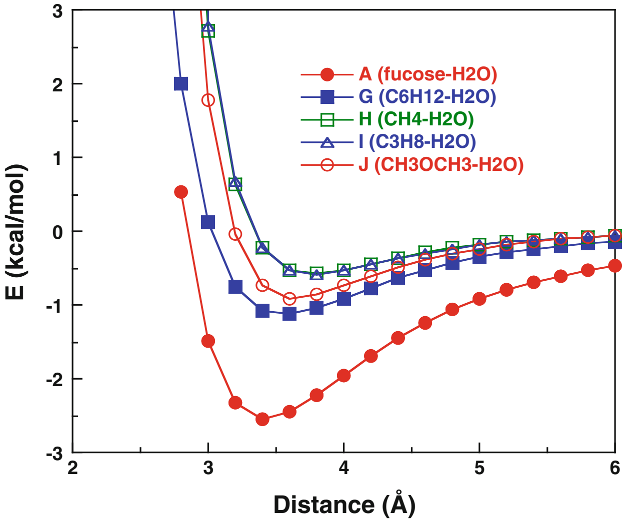

Fig. 6 Interaction energy potentials calculated for the fucose–water (**A**) and cyclohexane–water (**G**), methane–water (**H**), propane–water (**I**) and dimethylether–water (**J**) complexes at the MP2/aug-cc-pVTZ level. The geometries for the complexes are shown in Fig. 1

The E_{corr} for the fucose–water complex **A** (−1.45 kcal/mol) is close to that for the cyclohexane–water complex **G** (−1.29 kcal/mol), while the E_{es} for **A** (−1.54 kcal/mol) is significantly larger (more negative) than that for **G** (−0.11 kcal/mol). This shows that the electrostatic interactions are responsible for the larger interaction energy (E_{int}) for the fucose–water complex **A** compared with the cyclohexane–water complex **G**. The E_{corr} for **A** is close to the E_{es}, which suggests that both the electrostatic and dispersion interactions are responsible for the attraction in the fucose–water complex **A**. The contribution of the induction interactions (E_{ind}) to the attraction is small. On the other hand, the E_{es} for cyclohexane–water complex **G** is small. The large electron correlation contribution suggests that the dispersion interactions are the major source of the attraction in **G**. The nature of the CH/O interactions in the fucose–water complex is significantly different from that in the cyclohexane–water complex, which is a model of the CH/O interactions between saturated hydrocarbon and water. The electronegative oxygen atoms in fucose enhance the electrostatic interactions between the fucose and water. The charge distributions calculated for an isolated fucose show that the C–H bonds in the nonpolar surface of fucose have substantial positive charges. The calculated charges on the C_1–H, C_3–H and

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[3] The CH/O interaction energy calculated for the cyclohexane–water complex is significantly larger than that calculated for the methane–water complex. The larger dispersion interactions in the cyclohexane–water complex should be the cause of the larger interaction energy in the cyclohexane complex.

[4] Although the dispersion interactions contribute largely to the E_{corr}, the E_{corr} also includes some other terms such as the effects of intramolecular electron correlation on the electrostatic interactions.

Table 1 Electrostatic, induction and electron correlation contributions to the interaction energies for fucose–water and cyclohexane–water complexes

	E_{int}^{a}	E_{HF}^{b}	E_{es}^{c}	E_{ind}^{d}	E_{rep}^{e}	E_{corr}^{f}
Fucose–water **A**[g]	−2.55	−1.09	−1.54	−0.30	0.75	−1.45
Cyclohexane–water **G**[h]	−1.13	0.16	−0.11	−0.17	0.44	−1.29

Energy in kcal/mol. The geometries of complexes are shown in Fig. 1

[a] MP2/aug-cc-pVTZ level interaction energy

[b] HF/aug-cc-pVTZ level interaction energy

[c] Electrostatic energy. See text

[d] Induction energy. See text

[e] Repulsion energy (=$E_{HF} - E_{es} - E_{ind}$). See text

[f] Correlation interaction energy (=$E_{int} - E_{HF}$). E_{corr} is mainly dispersion energy. See text

[g] Intermolecular distance is 3.4 Å. See text

[h] Intermolecular distance is 3.6 Å. See text

C_5–H groups of fucose are 0.34, 0.27 and 0.35 *e* (1 *e* = 1.602 × 10^{-19} C), respectively.

The calculated interaction energy potentials for the fucose–water complex (orientations **A**, **D–F**) show that the charge–transfer interactions are not the major source of the attraction. The calculations show that substantial attraction still exists, even when the molecules are well separated. This shows that dispersion and electrostatic interactions are the major source of the attraction in the CH/O interactions in the fucose–water complex. The energies of these interactions behave as some inverse power of the distance ($E \sim R^{-n}$). The attraction should decrease exponentially with distance, if the contribution of the short–range interactions (charge–transfer interactions) to the attraction is significant, since the magnitude of the short–range interactions are approximately proportional to the magnitude of overlap integral [84].

3.6 SAPT calculations

The electrostatic, induction and dispersion energies for the fucose–water **A** and cyclohexane–water complexes **G** at the potential minima were also evaluated by DFT-SAPT calculations as summarized in Table 2. The $E_{es}^{(1)}$ for **A** (−2.79 kcal/mol) is significantly larger (more negative) than that for **G** (−0.75 kcal/mol), while the $E_{disp}^{(2)}$ for **A** and **G** (−1.62 and −0.99 kcal/mol) are not largely different. The SAPT calculations also show that the electrostatic interactions are responsible for the larger interaction energy for the fucose–water complex **A** compared with the cyclohexane–water complex **G**. The $E_{ind}^{(2)}$ for the complexes are negative, while the $E_{ex\text{-}ind}^{(2)}$ are positive. The total induction contributions (sum of the $E_{ind}^{(2)}$ and $E_{ex\text{-}ind}^{(2)}$) for the complexes A and G are not large (−0.47 and −0.28 kcal/mol, respectively).

4 Conclusion

The ab initio calculations of the CH/O interactions in the fucose–water complex provide important information for understanding the desolvation of carbohydrate molecules in water. The CH/O interactions in the fucose–water complex are significantly larger than those in the cyclohexane–water complex. This suggests that the CH/O interactions of carbohydrates are stronger than that of saturated hydrocarbons. The oxygen atoms in the fucose enhance the CH/O interactions between the C–H bonds in the nonpolar surface of fucose and water. The C–H groups in the nonpolar surface of fucose have substantial positive

Table 2 Electrostatic, induction and dispersion energies calculated for fucose–water and cyclohexane–water complexes by DFT-SAPT calculations

	$E_{es}^{(1)}$	$E_{ex}^{(1)}$	$E_{ind}^{(2)}$	$E_{ex\text{-}ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{ex\text{-}disp}^{(2)}$	E_{int}^{a}
Fucose–water **A**[b]	−2.79	3.69	−1.42	0.95	−1.62	0.28	−0.91
Cyclohexane–water **G**[c]	−0.75	1.69	−0.61	0.33	−0.99	0.13	−0.21

Energy in kcal/mol. The geometries of complexes are shown in Fig. 1. The cc-pVDZ basis set was used

[a] Total interaction energy. The sum of the six energy terms

[b] Intermolecular distance is 3.4 Å. See text

[c] Intermolecular distance is 3.6 Å. See text

charges. The electrostatic and dispersion interactions are responsible for the attraction between the nonpolar surface of fucose and water. On the other hand, the dispersion interaction is the major source of the attraction and the electrostatic contribution to the attraction is small in the cyclohexane–water complex. The calculations show that the nature of the CH/O interactions of carbohydrates is completely different from that of saturated hydrocarbons.

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