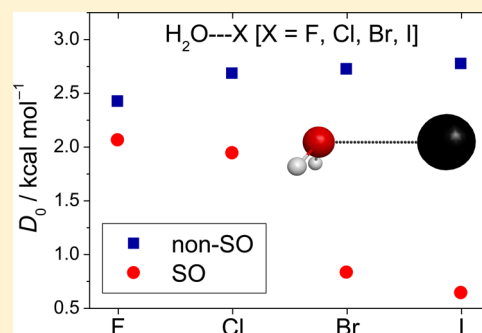


Surprising Quenching of the Spin–Orbit Interaction Significantly Diminishes H₂O⋯X [X = F, Cl, Br, I] Dissociation EnergiesGábor Czakó,^{*,†} Attila G. Császár,^{*,†,‡} and Henry F. Schaefer, III[§][†]Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary[‡]MTA-ELTE Research Group on Complex Chemical Systems, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary[§]Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, United States

ABSTRACT: The H₂O⋯X complexes, with X = F, Cl, Br, and I, show considerable viability with nonspin–orbit $D_e(D_0)$ dissociation energy values of 3.73(2.42), 3.60(2.68), 3.54(2.72), and 3.36(2.77) kcal mol⁻¹ for X = F, Cl, Br, and I, respectively, obtained at the CCSD(T)-F12b/aug-cc-pVTZ(-PP) level of theory using relativistic pseudopotentials (PPs) for Br and I. Spin–orbit (SO) corrections, computed with the Breit–Pauli operator in the interacting states approach at the all-electron MRCI+Q/aug-cc-pwCVTZ(-PP) level, are found to depend sensitively and unpredictably on the O⋯X separations. 96% (F), 87% (Cl), 54% (Br), and 30% (I) quenching of the SO corrections significantly reduces the dissociation energies of the H₂O⋯X complexes, resulting in $D_e(D_0)$ values of 3.38(2.06), 2.86(1.94), 1.64(0.83), and 1.23(0.64) kcal mol⁻¹ for X = F, Cl, Br, and I, respectively.



I. INTRODUCTION

Although the reactions of halogen atoms with water have been of interest for quite some time,^{1–3} new experiments⁴ and sophisticated computations^{5–14} reveal many important new features of these seemingly simple reactions. The recent H₂O⋯F⁻ photodetachment experiments of Continetti and co-workers⁴ were combined with thorough theoretical analysis to provide a new picture for the dynamics of the prototypical F + H₂O reaction.⁴ Similar experiments would be valuable for the analogous Cl, Br, and I atom systems.

From a theoretical perspective, it is obvious that as one goes down the periodic table from F + H₂O to I + H₂O, relativistic effects will become increasingly important. One feature of the related potential energy surfaces for which relativistic effects might seem unimportant is the dissociation energy for the entrance complexes H₂O⋯X. In these complexes the distances between the halogen atom and the water molecule are substantial, and it is not unreasonable to assume that the magnitude of the spin–orbit (SO) interaction of the entrance complex is about the same as that of the isolated halogen atom.

However, recent computations by Bowman and co-workers¹⁵ for the Br + H₂O system point to a rather different interpretation. Because their interest was in the HBr + OH reaction, they paid little attention to the H₂O⋯Br entrance well. Nevertheless, in a follow-up study of the same system, Zhang et al.⁷ noted that Bowman's results indicate a significant quenching of the H₂O⋯Br dissociation energy due to SO coupling. Zhang et al.⁷ expressed some surprise that the large equilibrium separation between Br and H₂O could alter the atomic SO coupling so much. In the present research, we address the dependence of the H₂O⋯X dissociation energies

for all the halogen atoms, i.e., for X = F, Cl, Br, and I. Our results do confirm the work of Bowman and co-workers¹⁵ qualitatively but contain some surprises for the other three systems.

II. COMPUTATIONAL DETAILS

The electronic structure computations performed utilize the aug-cc-pVnZ [n = D, T, and Q] and aug-cc-pwCVnZ [n = D and T] correlation consistent basis set family of Dunning and co-workers¹⁶ and small-core energy-consistent relativistic pseudopotentials (PPs) of the Stuttgart/Köln type¹⁷ with the corresponding aug-cc-pVnZ-PP [n = D, T, and Q] and aug-cc-pwCVnZ-PP [n = D and T] basis sets¹⁷ for Br and I. The PPs replace the inner-core electrons of Br (1s²2s²2p⁶) and I (1s²2s²2p⁶3s²3p⁶3d¹⁰), thereby accounting for the large scalar relativistic effects.

As to the level of electronic structure treatment, a variant of the restricted open-shell Hartree–Fock-based explicitly correlated unrestricted coupled cluster singles and doubles and perturbative triples method, ROHF-UCCSD(T)-F12b,¹⁸ is employed for the geometry optimizations and harmonic frequency computations and a multiconfigurational self-consistent field (MCSCF) method, a corrected multireference configuration interaction [MRCI+Q]^{19,20} method, and an explicitly correlated MRCI+Q [MRCI-F12+Q] method are

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Table 1. Equilibrium Structures (in Å and degrees) and Non-SO and SO-Corrected D_e and D_0 Values (in kcal mol⁻¹) for H₂O...X [X = F, Cl, Br, I]

basis ^c	non-SO (CCSD(T)-F12b) ^a						SO-corrected (AE-MRCI+Q) ^b					
	R(O...X)	R(OH)	α (HOX)	τ (HOXH)	D_e	Δ ZPE	D_0	X + H ₂ O	H ₂ O...X	Δ SO	D_e	D_0
	H ₂ O...F											
DZ	2.114	0.963	85.35	105.28	4.04	-1.23	2.81	-0.35	-0.01	-0.34	3.71	2.48
TZ	2.107	0.962	85.73	105.18	3.73	-1.31	2.42	-0.37	-0.01	-0.36	3.38	2.06
	H ₂ O...Cl											
DZ	2.563	0.962	95.53	105.47	3.86	-0.96	2.90	-0.82	-0.10	-0.73	3.13	2.17
TZ	2.586	0.961	96.59	105.78	3.60	-0.92	2.68	-0.84	-0.11	-0.73	2.86	1.94
	H ₂ O...Br											
DZ	2.744	0.961	100.56	107.36	3.65	-0.82	2.83	-3.43	-1.48	-1.95	1.70	0.87
TZ	2.757	0.961	100.56	107.35	3.54	-0.81	2.72	-3.51	-1.61	-1.90	1.64	0.83
	H ₂ O...I											
DZ	2.968	0.961	105.91	110.90	3.45	-0.72	2.73	-6.89	-4.61	-2.29	1.16	0.44
TZ	2.985	0.960	105.91	110.89	3.36	-0.59	2.77	-7.11	-4.98	-2.13	1.23	0.64

^aAll the complexes have C_s point-group symmetry. The ZPE corrections are based on harmonic frequencies obtained at the ROHF-UCCSD(T)-F12b/aug-cc-pVDZ(-PP) and ROHF-UCCSD(T)-F12b/aug-cc-pVTZ(-PP) levels of theory. ^bThe SO corrections, defined as the difference between the SO and non-SO ground-state electronic energies, are obtained at the AE-MRCI+Q(5,3)/aug-cc-pwCVDZ(-PP) and AE-MRCI+Q(5,3)/aug-cc-pwCVTZ(-PP) levels of theory. X + H₂O denotes the halogen atom SO corrections at large monomer separations, and H₂O...X denotes the entrance-complex SO corrections at the ROHF-UCCSD(T)-F12b/aug-cc-pVTZ(-PP) equilibrium geometries. ^cDZ and TZ denote aug-cc-pVDZ(-PP) and aug-cc-pVTZ(-PP), respectively, for the non-SO and aug-cc-pwCVDZ(-PP) and aug-cc-pwCVTZ(-PP), respectively, for the SO computations (PPs and the corresponding PP basis sets are used for Br and I).

used for the SO computations. The Davidson correction²¹ (+Q) is used to estimate higher-order correlation energy effects. All the single-reference electronic structure computations employ the usual frozen-core (FC) approach, whereas both the FC and all-electron (AE) approaches are used for the multireference computations. Note that in the AE computations the outer-core electrons, i.e., (1s²) for O and F, (2s²2p⁶) for Cl, (3s²3p⁶3d¹⁰) for Br, and (4s²4p⁶4d¹⁰) for I, as well as the valence electrons are correlated. A minimal active space of 5 electrons in the three spatial *np*-like orbitals, where *n* = 2, 3, 4, and 5 for F, Cl, Br, and I, respectively, and a large full-valence active space of 15 electrons in 10 spatial orbitals are used for the multireference computations. The SO computations employ the Breit–Pauli operator in the interacting-states approach.²² The SO eigenstates are obtained by diagonalizing a 6 × 6 SO matrix, whose diagonal elements are replaced by the Davidson-corrected MRCI or MRCI-F12 energies, except for MCSCF. All the electronic structure computations are performed with the help of the *ab initio* program package MOLPRO.²³

III. RESULTS AND DISCUSSION

Structural parameters and non-SO and SO dissociation energies (both D_e and D_0) of the H₂O...X [X = F, Cl, Br, I] complexes are reported in Table 1. The CCSD(T)-F12b method converges remarkably well with respect to basis size: the aug-cc-pVDZ and aug-cc-pVTZ Born–Oppenheimer equilibrium geometry parameter estimates agree within 0.001 Å for the intramolecular OH bond length and within about 0.02 Å for the more sensitive intermolecular O...X distances. The dissociation energies decrease by only about 0.1–0.3 kcal mol⁻¹ if the basis is increased from DZ to TZ. Thus, knowing the fast convergence of the F12 methods, we can be confident that the aug-cc-pVTZ relative energies are converged to within about 0.1 kcal mol⁻¹. The post-CCSD(T) electron correlation effect, the core–valence correlation effect, and the scalar relativistic effect on H, O, F, and Cl and the error of the PP approximation for Br and I are expected to be small. For

example, it is stated in ref 15 that the above auxiliary corrections for H₂O...Br are 0.02, 0.08, and 0.00 kcal/mol, respectively. Note that the use of PP accounts for the scalar relativistic effect on Br; thus, the 0.00 kcal/mol correction corresponds to the scalar relativistic effect on H and O and the inaccuracy of the PP approximation.¹⁵

The equilibrium O...X distances are 2.107, 2.586, 2.757, and 2.985 Å for X = F, Cl, Br, and I, respectively, and the corresponding D_e values without SO coupling are in the same ballpark at 3.73, 3.60, 3.54, and 3.36 kcal mol⁻¹. For X = F and Cl the present D_e values agree with those of Guo and co-workers,¹⁴ as they used the same level of electronic structure theory. For X = Br, Guo and co-workers¹⁴ reported a slightly different D_e of 3.47 kcal mol⁻¹, because they did not employ a pseudopotential for Br. Here a D_e of 3.54 kcal mol⁻¹ has been obtained with PP and the corresponding aug-cc-pVTZ-PP basis set. As seen, the O...X equilibrium distances increase and the D_e values slightly decrease as we go from X = F to X = I. As the binding gets looser, the harmonic zero-point vibrational energies (ZPEs) of the H₂O...X complexes decrease, the ZPEs are 5172, 5035, 4997, and 4920 cm⁻¹ for X = F, Cl, Br, and I, respectively, whereas the ZPE of H₂O is 4713 cm⁻¹. As a result, the ZPE corrections significantly decrease the dissociation energies, for H₂O...F by 1.31 kcal mol⁻¹ and the absolute ZPE effects become smaller and smaller: 0.92, 0.81, and 0.59 kcal mol⁻¹ for X = Cl, Br, and I, in order. Therefore, the ZPE corrections reverse the order of the dissociation energies. In other words, unlike the D_e values, the D_0 values slightly increase from X = F to I, they are 2.42, 2.68, 2.72, and 2.77 kcal mol⁻¹ for X = F, Cl, Br, and I, respectively. At this point, the present D_e and D_0 values agree well with previous theoretical predictions.^{5–8,14} However, most of the previous studies did not consider the SO effects on the dissociation energies.

To understand the SO effects on the dissociation energies of the H₂O...X [X = F, Cl, Br, I] complexes, we computed one-dimensional non-SO and SO potential energy curves as a function of the O...X distance, maintaining the C_s point-group symmetry and keeping the other internal coordinates (R_{OH} ,

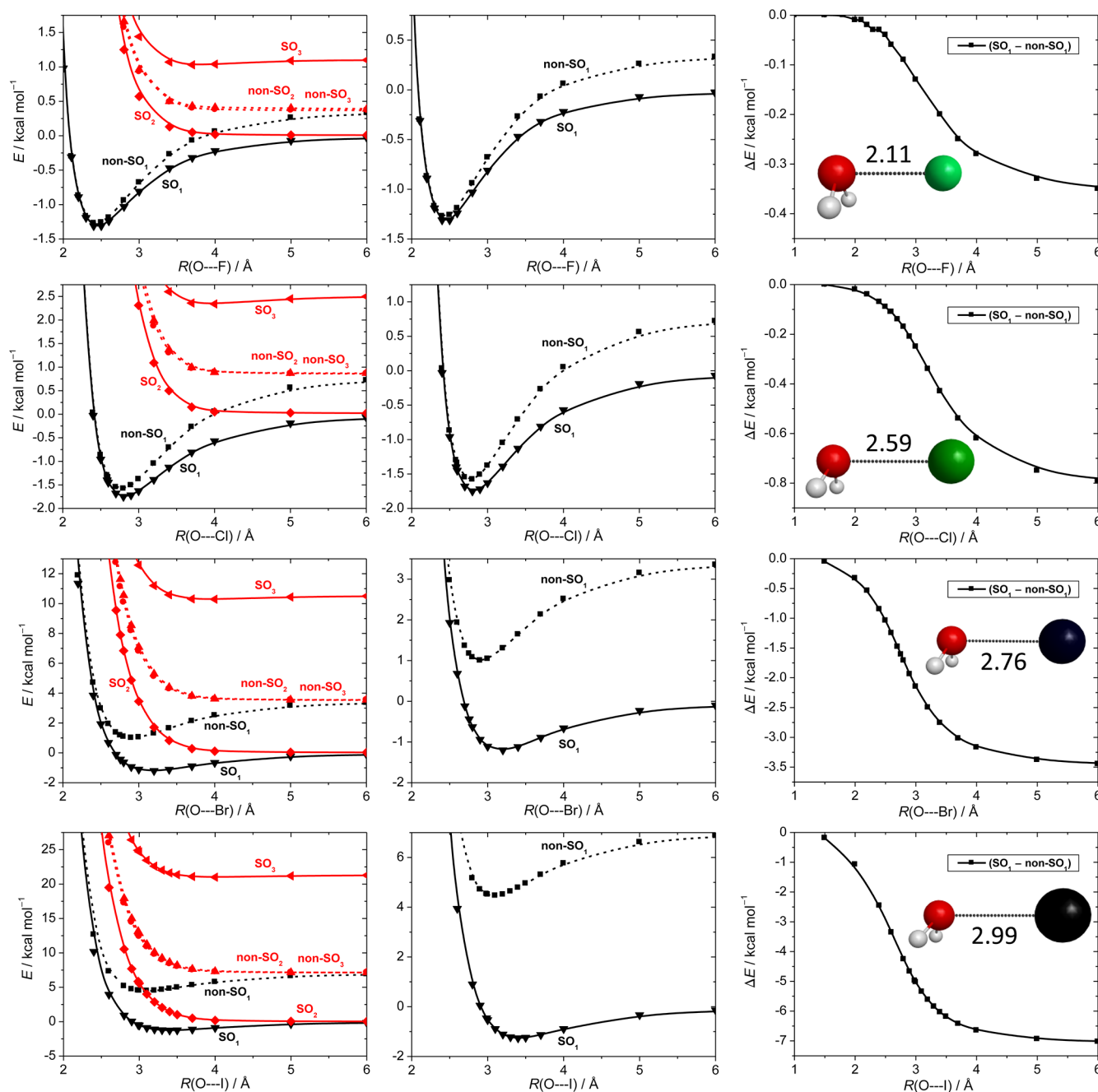


Figure 1. Potential energy curves obtained at the AE-MRCI+Q(5,3)/aug-cc-pwCVTZ(-PP) (PPs for Br and I) level as a function of the $\text{H}_2\text{O}\cdots\text{X}$ [$\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$] separation, keeping the H_2O unit at the CCSD(T)-F12b/aug-cc-pVTZ(-PP) equilibrium structure corresponding to the entrance-channel complex (C_s). SO_1 and non- SO_1 (black curves) denote the spin-orbit (SO) and non-SO ground electronic states, respectively, whereas the red curves correspond to excited states. In the right panels the energy differences between the SO and non-SO ground states are shown as a function of the $\text{O}\cdots\text{X}$ distance.

α_{HOX} , τ_{HOXH}) fixed at their equilibrium values corresponding to the $\text{H}_2\text{O}\cdots\text{X}$ minima. Figure 1 shows the potentials for the non-SO ground electronic state and the two quasi-degenerate excited electronic states, which are not reactive within an adiabatic approximation. All three non-SO states correlate with the $\text{X}(^2\text{P}) + \text{H}_2\text{O}$ asymptote. The SO coupling splits the ground state of the X atom (^2P) to a 4-fold degenerate SO ground state ($^2\text{P}_{3/2}$) and a 2-fold degenerate SO excited state ($^2\text{P}_{1/2}$). As X approaches H_2O , the 4-fold degenerate state splits into two doubly degenerate SO states (Figure 1, left panels).

As seen in Figure 1 (middle panels), the non-SO and SO-corrected ground-state potentials approach each other as the $\text{O}\cdots\text{X}$ distance decreases and the two curves merge at an $\text{O}\cdots\text{X}$ separation around 1.5–2.5 Å. Our interest is in the energy difference between the SO and non-SO ground electronic states, $\Delta E_{\text{SO}} = E_{\text{SO}} - E_{\text{non-SO}}$, because the $\Delta E_{\text{SO}}(\text{X}) - \Delta E_{\text{SO}}(\text{H}_2\text{O}\cdots\text{X})$ values are the SO corrections for the dissociation energies. As Figure 1 (right panels) shows, the SO corrections depend very sensitively on the $\text{O}\cdots\text{X}$ separations. The absolute ΔE_{SO} decreases steeply, especially between $\text{O}\cdots\text{X}$ distances of 4 and 2 Å, as X approaches H_2O ,

Table 2. Spin–Orbit Corrections (in kcal mol⁻¹) at Different Levels of Theory for X + H₂O and H₂O...X [X = F, Cl, Br, I]^a

level of theory ^b	F + H ₂ O	H ₂ O...F	ΔSO	Cl + H ₂ O	H ₂ O...Cl	ΔSO	Br + H ₂ O	H ₂ O...Br	ΔSO	I + H ₂ O	H ₂ O...I	ΔSO
MCSCF(5,3)/aVDZ	-0.36	-0.02	-0.34	-0.78	-0.09	-0.69	-3.35	-1.45	-1.90	-6.94	-4.63	-2.31
MCSCF(5,3)/aVTZ	-0.37	-0.02	-0.35	-0.78	-0.10	-0.68	-3.35	-1.50	-1.86	-6.92	-4.71	-2.21
MCSCF(5,3)/aVQZ	-0.38	-0.02	-0.36	-0.78	-0.10	-0.69	-3.36	-1.50	-1.86	-6.93	-4.73	-2.20
MCSCF(15,10)/aVDZ	-0.36	-0.02	-0.34	-0.78	-0.08	-0.70	-3.35	-1.37	-1.98	-6.94	-4.50	-2.44
MCSCF(15,10)/aVTZ	-0.37	-0.02	-0.35	-0.78	-0.09	-0.69	-3.35	-1.40	-1.95	-6.92	-4.57	-2.35
MRCI+Q(5,3)/aVDZ	-0.34	-0.01	-0.33	-0.75	-0.08	-0.67	-3.22	-1.29	-1.93	-6.66	-4.33	-2.32
MRCI+Q(5,3)/aVTZ	-0.37	-0.01	-0.35	-0.76	-0.08	-0.68	-3.25	-1.39	-1.86	-6.67	-4.52	-2.15
MRCI+Q(5,3)/aVQZ	-0.38	-0.01	-0.36	-0.76	-0.08	-0.68	-3.27	-1.40	-1.87	-6.73	-4.56	-2.16
MRCI+Q(15,10)/aVDZ	-0.34	-0.01	-0.33	-0.76	-0.07	-0.69	-3.28	-1.28	-2.00	-6.76	-4.33	-2.43
MRCI+Q(15,10)/aVTZ	-0.37	-0.01	-0.36	-0.77	-0.08	-0.69	-3.30	-1.36	-1.94	-6.78	-4.50	-2.28
MRCI-F12+Q(5,3)/aVDZ	-0.35	-0.01	-0.34	-0.76	-0.08	-0.68	-3.29	-1.40	-1.88	-6.80	-4.63	-2.17
MRCI-F12+Q(5,3)/aVTZ	-0.37	-0.01	-0.35	-0.76	-0.09	-0.68	-3.27	-1.40	-1.87	-6.72	-4.55	-2.17
MRCI-F12+Q(5,3)/aVQZ	-0.38	-0.01	-0.36	-0.77	-0.09	-0.68	-3.28	-1.40	-1.88	-6.74	-4.57	-2.17
MRCI-F12+Q(15,10)/aVDZ	-0.35	-0.01	-0.34	-0.77	-0.08	-0.69	-3.31	-1.38	-1.94	-6.84	-4.60	-2.24
MRCI-F12+Q(15,10)/aVTZ	-0.37	-0.01	-0.36	-0.77	-0.08	-0.69	-3.31	-1.37	-1.94	-6.81	-4.53	-2.28
AE-MRCI+Q(5,3)/awCVDZ	-0.35	-0.01	-0.34	-0.82	-0.10	-0.73	-3.43	-1.48	-1.95	-6.89	-4.61	-2.29
AE-MRCI+Q(5,3)/awCVTZ	-0.37	-0.01	-0.36	-0.84	-0.11	-0.73	-3.51	-1.61	-1.90	-7.11	-4.98	-2.13
experiment ^c												
				-0.84			-3.51			-7.25		

^aThe SO corrections are defined as the difference between the SO and non-SO ground-state electronic energies, $E_{\text{SO}} - E_{\text{non-SO}}$. F, Cl, Br, and I + H₂O denote the SO corrections for the corresponding F, Cl, Br, and I + H₂O asymptotic limits and H₂O...F, H₂O...Cl, H₂O...Br, and H₂O...I denote the entrance-complex SO corrections at the ROHF-UCCSD(T)-F12b/aug-cc-pVTZ(-PP) equilibrium geometries. ΔSO denotes the SO corrections for the dissociation energies. ^baVDZ, aVTZ, and aVQZ denote the corresponding aug-cc-pVnZ(-PP) [n = D, T, and Q] bases and awCVDZ and awCVTZ denote the corresponding aug-cc-pwCVnZ(-PP) [n = D and T] basis sets. PPs and the corresponding PP basis sets are used for Br and I. (5,3) and (15,10) denote active spaces of 5 electrons in 3 orbitals and 15 electrons in 10 orbitals, respectively. For further details see text. ^cExperimental data are obtained from the measured atomic SO splittings of $\epsilon = 1.16(\text{F}), 2.52(\text{Cl}), 10.54(\text{Br}),$ and $21.74(\text{I})$ kcal mol⁻¹, as $-\epsilon/3$.³⁰

and almost completely quenches at a 1.5 Å O...X separation. Because the equilibrium O...X distances of the H₂O...X complexes are in the 2–3 Å range, the $\Delta E_{\text{SO}}(\text{H}_2\text{O}\cdots\text{X})$ corrections are not equal to the $\Delta E_{\text{SO}}(\text{X})$ values for the X + H₂O asymptotic limits; thus, significant SO effects on the dissociation energies are expected. In the cases of H₂O...F and H₂O...Cl, which have the shortest O...X equilibrium distances of 2.11 and 2.59 Å, respectively, the ΔE_{SO} corrections are almost completely quenched (−0.01 and −0.11 kcal mol⁻¹, respectively). Thus, the corresponding dissociation energies are lowered by 0.36 and 0.73 kcal mol⁻¹, these values are almost equal to the atomic SO corrections. For H₂O...Br the quenching of ΔE_{SO} is also substantial, because $\Delta E_{\text{SO}}(\text{H}_2\text{O}\cdots\text{Br}) = -1.61$ kcal mol⁻¹, whereas $\Delta E_{\text{SO}}(\text{Br}) = -3.51$ kcal mol⁻¹; thus, the dissociation energy is significantly reduced by 1.90 kcal mol⁻¹. As expected, the O...X separation is the largest in H₂O...I (2.99 Å), but even at this large distance ΔE_{SO} is −4.98 kcal mol⁻¹. As the atomic correction is −7.11 kcal mol⁻¹, there is a large decrease of the dissociation energy by 2.13 kcal mol⁻¹.

We have investigated the dependence of the above-described SO corrections upon the level of electronic structure theory, shown in Table 2. A TZ basis with a minimal active space provides reasonably accurate results, because the aug-cc-pVTZ and aug-cc-pVQZ SO corrections agree within 0.06 kcal mol⁻¹ (or even better with F12) and the minimal and full-valence active spaces give the same results within 0.12 kcal mol⁻¹. A more significant effect is found when we correlate the core electrons, especially for X = Br and I, where the $\Delta E_{\text{SO}}(\text{X})$ values change by 0.26 and 0.44 kcal mol⁻¹, respectively, thereby improving the agreement with experiment, as shown in Table 2. It is important to note that if we consider the $\Delta E_{\text{SO}}(\text{X}) - \Delta E_{\text{SO}}(\text{H}_2\text{O}\cdots\text{X})$ corrections, which are the real interest of the present study, the core-correlation effects are less than 0.06 kcal mol⁻¹ for all cases. Because the all-electron results give the best agreement with the measured atomic SO splittings, we use the

AE-MRCI+Q(5,3)/aug-cc-pwCVTZ SO corrections to compute the final estimates for the dissociation energies.

Applying the SO corrections to the dissociation energies, we get D_e values of 3.38, 2.86, 1.64, and 1.23 kcal mol⁻¹ for H₂O...X with X = F, Cl, Br, and I, respectively, whereas the corresponding D_0 values are reduced to 2.06, 1.94, 0.83, and 0.64 kcal mol⁻¹, in order. Clearly, the SO corrections substantially reduce the dissociation energies. Even if the quenching of ΔE_{SO} is most significant for the complex H₂O...F, the SO correction has the largest effect on the dissociation energy of H₂O...I, because the SO splitting of iodine is an order of magnitude larger than that of fluorine. For H₂O...Br the present SO-corrected D_e value of 1.64 kcal mol⁻¹ confirms the recent prediction of Bowman and co-workers,¹⁵ 1.62 kcal mol⁻¹.

Because the magnitude of the SO correction depends sensitively on the O...X separation, the SO coupling affects the position of the minima (Figure 1). This geometry effect is negligible for X = F and Cl, but substantial (about +0.3 Å) for X = Br and I, as seen in Figure 1 (middle panels). Note also that MRCI+Q overestimates the CCSD(T)-F12b equilibrium O...X distances by about 0.1–0.2 Å if a minimal active space is employed for MRCI, because CCSD(T)-F12b provides a much more accurate description of the dynamical electron correlation. If we use the large full-valence active space, MRCI+Q reproduces well the CCSD(T) geometries for X = Cl, Br, and I, indicating that static electron correlation is not significant at the H₂O...X minima, except for H₂O...F. The T_1 diagnostic²⁴ further supports the above findings, because $T_1 = 0.033$ for H₂O...F, whereas for X = Cl, Br, and I the T_1 diagnostic values of 0.017, 0.013, and 0.010, respectively, are well below 0.02, indicating that single-reference correlation methods can describe the H₂O...X [X = Cl, Br, and I] complexes well.

Due to the large dipole moment of H₂O and the covalent nature of the O...X bond,¹⁴ the H₂O...X complexes are expected to be much more stable than the corresponding CH₄...X complexes. In the case of the CH₄...X complexes the shallower minima correspond to single-H-bonded H₃CH...X (C_{3v}) structures and deeper minima were found at the HCH₃...X (C_{3v}) arrangements.^{25–29} Without SO corrections the D_e values for the H₃CH...X complexes are about 0.3 kcal mol⁻¹, whereas HCH₃...X have D_e of about 0.9 kcal mol⁻¹.^{25–29} These D_e values are indeed much smaller than the corresponding H₂O...X dissociation energies. However, due to the much larger C...X separations at H₃CH...X (R_{CX} = 3.5–4.5 Å) as compared to the corresponding O...X distances (R_{OX} = 2.0–3.0 Å), the SO effects are negligible for the dissociation energies of H₃CH...X.^{25–29} For HCH₃...X, where the C...X distances are in the range 3.0–4.0 Å, the SO corrections are slightly quenched, thereby decreasing the dissociation energies by about 0.3 kcal mol⁻¹, resulting in D_e values of about 0.6 kcal mol⁻¹.^{25–28} Thus, for X = F and Cl the H₂O...X complexes are indeed much more strongly bound than the corresponding CH₄...X complexes. However, for X = Br and I, where the large quenching of the SO corrections significantly diminishes the H₂O...X dissociation energies, the H₂O...X and CH₄...X complexes have comparable dissociation energies.

IV. SUMMARY AND CONCLUSIONS

Several dynamical studies have shown that entrance-channel complexes may play important steering roles in the dynamics of bimolecular chemical reactions, thereby influencing the outcome of the reactions.^{9,26} H₂O forms promising complexes with halogen atoms F, Cl, Br, and I, whereby the D_e and D₀ values vary in the ranges of 3.3–3.8 and 2.4–2.8 kcal mol⁻¹, respectively, if SO interactions are not considered. It is well-known that SO coupling lowers the reactant asymptote of the X + H₂O reactions by the SO correction of the halogen atom. For an entrance-channel complex, one may expect that the SO correction at the geometry of the complex is the same as the atomic limit; thus, there may be no effect on the dissociation energy. The present study shows, however, that 96, 87, 54, and 30% of the atomic SO corrections, defined as E_{SO} - E_{non-SO}, are quenched for the H₂O...X complexes, where X = F, Cl, Br, and I, respectively, thereby reducing the dissociation energies by 0.36, 0.73, 1.90, and 2.13 kcal mol⁻¹, in order. (Note that unlike E_{SO} - E_{non-SO}, the measurable SO splittings between the lowest and highest SO states, defined as E_{SO}(excited) - E_{SO}(ground), increase as X approaches H₂O.) Though the percentage-wise quenching of (E_{SO} - E_{non-SO}) is getting smaller from X = F to I, the SO effects on the dissociation energies are more and more substantial if we go down the periodic table, because the atomic SO corrections increase rapidly from F to I. Whereas the non-SO D₀ values are similar for all the H₂O...X complexes, the SO-corrected D₀ values are 2.06, 1.94, 0.83, and 0.64 kcal mol⁻¹ for X = F, Cl, Br, and I, respectively.

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Notes

The authors declare no competing financial interest.

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