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## Systematic characterization of the homogeneous and heterogeneous hydrogen halide dimers

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This study systematically characterizes the 4 homogeneous and 6 heterogeneous hydrogen-bonded dimers formed by hydrogen halide pairs (HX/HY where X,Y = F, Cl, Br and I). The notation  $\text{HX}\cdots\text{HY}$  indicates the direction of the hydrogen bond from the HY donor to the HX acceptor. All stationary points reported for these 10 dimer systems are fully optimized utilizing the MP2 and CCSD(T) *ab initio* methods in conjunction with quadruple- $\zeta$  correlation-consistent basis sets augmented with diffuse functions, and their nature is verified by harmonic vibrational frequency computations. The electronic dissociation energies ( $D_e$ ) for all 10 global minima are evaluated near the CCSD(T) complete basis set (CBS) limit via extrapolation schemes. These values are 19.11, 8.32, 7.38 and 6.22 kJ mol<sup>-1</sup> for the homogeneous dimers of HF, HCl, HBr and HI, respectively. For the heterogeneous pairs, the lighter hydrogen halide is consistently the donor in the global minimum configuration, with  $D_e$  ranging from 12.23 kJ mol<sup>-1</sup> for HCl $\cdots$ HF to 7.22 kJ mol<sup>-1</sup> for HI $\cdots$ HBr near the CCSD(T) CBS limit. Interestingly, not all heterodimer donor/acceptor permutations correspond to minima. For example, the HCl $\cdots$ HBr configuration is identified as a local minimum at all levels of theory employed in this investigation, whereas the in-plane barrier for donor/acceptor exchange vanishes for HCl $\cdots$ HI and HBr $\cdots$ HI when larger quadruple- $\zeta$  basis sets are utilized. For the 7 dimer systems containing Br and/or I, the structures, energetics and vibrational frequencies computed using conventional valence-only electron correlation procedures are similar to those obtained using an expanded valence treatment that includes the (n-1)*d* subvalence electrons associated with Br and I.

## I. INTRODUCTION

The hydrogen bond is a strong and highly directional non-covalent interaction that can be widely observed in nature.<sup>1-4</sup> Hydrogen bonding has been intensely studied and broadly applied in different chemistry fields, including biomedical materials, drug delivery,<sup>5-8</sup> crystal design,<sup>9-12</sup> solution chemistry,<sup>13-15</sup> and polymer science.<sup>16-18</sup> Hydrogen halides are simple diatomic molecules with one hydrogen atom directly bonded to an electronegative halogen (H-X, where X = F, Cl, Br and I), and they have provided important platforms for the detailed interrogation of hydrogen bonding, both experimentally and theoretically.<sup>19</sup> The polar diatomic structure allows HX monomers to undergo extensive self-association and form oligomeric (HX)<sub>m</sub> clusters through hydrogen bonds. Over the past four decades, the small homogeneous (HX)<sub>m</sub> cyclic clusters (where  $m = 3-6$  when X = F and Cl, and  $m = 3-5$  when X = Br and I) have been characterized and a number of studies have probed the cooperative effects of hydrogen bonding in these systems.<sup>20-37</sup> The enhanced attractive interactions in (HX)<sub>m</sub> cyclic clusters are evident through their larger dissociation energies ( $D_e$ ) per hydrogen bond compared to the corresponding HX dimers.<sup>38-42</sup> Numerous studies have reported the  $D_e$  of homogenous (HX)<sub>2</sub> structures. The strongest hydrogen bond is observed in (HF)<sub>2</sub> with a  $D_e$  of *ca.* 18 kJ mol<sup>-1</sup>.<sup>43-52</sup> In contrast, (HCl)<sub>2</sub> has a much smaller  $D_e$  of *ca.* 9 kJ mol<sup>-1</sup>.<sup>51,53-56</sup> Investigations of the heavier (HBr)<sub>2</sub> and (HI)<sub>2</sub> analogs have revealed that the  $D_e$  consistently decreases down the period for this hydrogen halide series (*ca.* 6 kJ mol<sup>-1</sup> for the former and *ca.* 5 kJ mol<sup>-1</sup> for the latter).<sup>51,52,57-62</sup>

The heterogeneous hydrogen halides dimers have also been characterized in a number of computational studies,<sup>56,61-72</sup> and several pairs have been observed experimentally.<sup>38,73-79</sup> In this study we have adopted the notation HX/HY for these heterogeneous systems along with HX...HY to distinguish between the different hydrogen bond acceptor...donor configurations, where X, Y = F, Cl, Br, I but X ≠ Y. (This notation is also sometimes used when X=Y for the homogeneous (HX)<sub>2</sub> systems.) The energetic trend favoring the heavier halogen in the hydrogen bond acceptor position for this heterogeneous series was noted as early as 1988 in a study published by Buckingham and Fowler that employed an electrostatic model based on charge densities from SCF computations on the monomers.<sup>68</sup> Subsequent investigations over the past three decades have reported results consistent with that qualitative observation,<sup>69</sup> including some recently reported CCSD(T) energetics obtained near the complete basis set (CBS) limit.<sup>61,62,72</sup> To the best of our knowledge, however, there has never been a systematic examination of both acceptor...donor configurations for all 6

heterogeneous dimers with *ab initio* quantum chemistry techniques based on wave function theory or density functional theory.

Accurate hydrogen bond strengths for these HX/HY systems provide important reference data, especially for the analysis of cooperative effects in larger homo- and heterogeneous hydrogen halide clusters. In this study we utilized MP2 and CCSD(T) *ab initio* methods and revisited this series of hydrogen-bonded dimers. Because recent studies have recognized the potentially non-negligible role of the (n-1)*d* electrons in non-covalent interactions involving Br and I (both hydrogen and halogen bonding),<sup>80</sup> our MP2 and CCSD(T) computations utilized not only the standard valence-only electron correlation procedure but also an expanded valence treatment that includes the 3*d* electrons of Br and 4*d* electrons for I. Large quadruple- $\zeta$  correlation consistent basis sets were used in conjunction with the aforementioned *ab initio* methods to optimize the HX/HY minima and also characterize the in-plane hydrogen bond exchange pathways between the two different HX...HY configurations of the heterogeneous dimers. Additional single-point CCSD(T) energies were computed to determine the dissociation and relative energies of the minima near the CBS limit.

## II. COMPUTATIONAL DETAILS

All dimer structures and their associated monomers reported in this manuscript were fully optimized using second-order Møller-Plesset perturbation theory (MP2)<sup>81</sup> and the CCSD(T)<sup>82-84</sup> coupled-cluster method method in conjunction with polarized valence correlation-consistent basis sets augmented with diffuse functions. They are simply denoted as "a*NZ*" where *N* = D, T and Q, and consist of aug-cc-p*VNZ* for H and F,<sup>85-87</sup> aug-cc-p*V(N+d)Z* for Cl,<sup>88</sup> and aug-cc-p*VNZ-PP* for Br and I (where the 10 and 28 inner-core electrons were replaced with the corresponding relativistic mixed density fitting (MDF) pseudopotential, respectively).<sup>89,90</sup> For systems containing Br and I, the analogous core-valence basis sets (aug-cc-pw*CVNZ-PP*, abbreviated as a*CVNZ*) were also employed.<sup>91</sup> The 1*s*-like orbitals of F and the 1*s*-, 2*p*-, and 2*p*-like orbitals of Cl were excluded from all MP2 and CCSD(T) electron correlation procedures. For Br and I, all computations with the a*VNZ* basis sets froze all subvalence *s*-, *p*- and *d*-like orbitals (3*s*-, 3*p*- and 3*d*-like orbitals for Br and 4*s*-, 4*p*- and 4*d*-like orbitals for I). In contrast, computations with the core-valence a*CVNZ* basis sets expanded beyond a valence-only treatment by including the (n-1)*d*-like orbitals of Br and I in the electron correlation procedure (only freezing 3*s* and 3*p* on Br and 4*s*

and  $4p$  on I). For the heterogeneous HX/HY dimers, the structures of the planar transition states connecting two different donor/acceptor configurations have also been optimized with the same methods and basis sets.

The nature of each stationary point was confirmed via harmonic vibrational frequency computations at the same level of theory (1 imaginary frequency for the transition states and 0 for the minima). Gradients and Hessians were obtained analytically for all MP2 structures. Analytic gradients were also available for the CCSD(T) optimizations, but the corresponding Hessians were obtained numerically from finite differences of analytic gradients. The Cartesian forces of the optimized structures did not exceed  $1.0 \times 10^{-6} E_h/a_0$ .

In each heterogeneous HX/HY pair, the relative electronic energy ( $\Delta E$ ) of the local minimum configuration and electronic barrier height associated with the planar transition state connecting the two different donor/acceptor configuration ( $\Delta E^*$ ) were defined relative to the global minimum. Based on the fully optimized structures of the dimers and individual fragments, dissociation energies ( $D_e$ ) of the 10 global minima (4 homogeneous and 6 heterogeneous) were determined by subtracting the electronic energy of the hydrogen-bonded dimer from the sum of the electronic energies of the corresponding isolated monomers. Additionally, these  $D_e$  values were determined near the CCSD(T) CBS limit using separate algebraic expressions to extrapolate the Hartree-Fock energy ( $E_{\text{HF}}$ ) and correlation energy ( $E_c$ ) from aCVNZ single-point energies (where  $N = 3, 4, 5$ ) computed using the corresponding CCSD(T)/aCVQZ optimized structures.<sup>92-94</sup> The CBS-limit Hartree-Fock energy ( $E_{\text{HF}}^{\text{CBS}}$ ) was obtained from the three-parameter exponential function proposed by Feller<sup>95</sup> with the three largest basis set series ( $N = T, Q, 5$ ).

$$E_{\text{HF}}^{\text{CBS}} = E_{\text{HF}}^{5Z} - \frac{(E_{\text{HF}}^{5Z} - E_{\text{HF}}^{\text{QZ}})^2}{E_{\text{HF}}^{\text{TZ}} - 2E_{\text{HF}}^{\text{QZ}} + E_{\text{HF}}^{5Z}} \quad (1)$$

Similarly, using the two largest basis sets ( $X = Q$  and 5), the CBS-limit electronic correlation energy ( $E_c^{\text{CBS}}$ ) was computed using the two-parameter inverse-cubic function described by Helgaker and co-workers using the two largest basis sets ( $X = Q$  and 5).<sup>96</sup>

$$E_c^{\text{CBS}} = \frac{5^3 E_c^{5Z} - 4^3 E_c^{\text{QZ}}}{61} \quad (2)$$

The counterpoise procedure (CP)<sup>97-99</sup> was not used to compute  $D_e$  because the inconsistency commonly referred to as basis set superposition error (BSSE)<sup>100,101</sup> must vanish in the limit of a complete basis set. All MP2 calculations were performed with Gaussian16<sup>102</sup> and all CCSD(T)

calculations were performed with CFOUR.<sup>103</sup>

### III. RESULTS AND DISCUSSION

#### A. Homogeneous (HX)<sub>2</sub> Global Minima

The optimized (HX)<sub>2</sub> structures reported here are consistent with those previously reported, and all minima are in C<sub>s</sub> point group symmetry. The optimized CCSD(T) electronic structures obtained with the aQZ and aCVQZ basis sets indicate that  $\theta(\text{X}\cdots\text{H}-\text{Y})$  is always under 170 for homogeneous (HX)<sub>2</sub>. In contrast, the  $\theta(\text{H}-\text{X}\cdots\text{H})$  is always *ca.*  $87 \pm 5$  except for HF $\cdots$ HF where it is *ca.* 114. As can be seen from the data collected in Table I, the expanded valence treatment with the aCVQZ basis set produces noticeably shorter covalent bond lengths than the conventional valence correlation procedures with the aQZ basis set (by *ca.* 0.006 Å for (HBr)<sub>2</sub> and more than 0.010 Å for (HI)<sub>2</sub>). However, the same trend is observed in the isolated monomers, and as a result, both procedures predict nearly identical bond length changes upon dimerization. Compared with the isolated monomer, elongation of the covalent bond was observed in both hydrogen bond donor and acceptor in each (HX)<sub>2</sub> minimum, and these  $\Delta R$  values are reported in Table II. For HF $\cdots$ HF, HCl $\cdots$ HCl, HBr $\cdots$ HBr and HI $\cdots$ HI, the changes in covalent bond lengths of the acceptor fragments ( $\Delta R(\text{H}-\text{X})$ ) are *ca.* 0.002, 0.006, 0.010 and 0.013 Å, whereas the changes in covalent bond lengths of the donor fragments ( $\Delta R(\text{H}-\text{Y})$ ) are always slightly larger with values of *ca.* 0.005, 0.008, 0.012 and 0.016 Å, respectively. The Cartesian coordinates of the fully optimized (HX)<sub>2</sub> and isolated HX monomers can be found in the Supplementary Material.

As expected from prior computational results reported for the 4 homogeneous dimers, the  $D_e$  decreases monotonically down the halide group: (HF)<sub>2</sub> > (HCl)<sub>2</sub> > (HBr)<sub>2</sub> > (HI)<sub>2</sub>. The  $D_e$  of (HF)<sub>2</sub> is 19.77 kJ mol<sup>-1</sup> at the CCSD(T)/aQZ level of theory. Although this result deviates by only 0.44 kJ mol<sup>-1</sup> from the CCSD(T) CBS value reported by Řezáč<sup>61,62</sup> (last column of Table III), the difference is reduced by nearly a factor of 2 for the a5Z single point energy computations and subsequent CBS extrapolations using the aQZ optimized geometries. The hydrogen bond is much weaker in (HCl)<sub>2</sub> which has a  $D_e$  of 8.56 kJ mol<sup>-1</sup> at CCSD(T)/aQZ level of theory. The extrapolated CCSD(T)  $D_e$  obtained here lies within 0.08 kJ mol<sup>-1</sup> of the previously reported CBS value.<sup>61,62</sup>

Moving down the hydrogen halide series to (HBr)<sub>2</sub> and (HI)<sub>2</sub>, the  $D_e$  continues to decrease sys-

tematically, but the changes are less precipitous. At the CCSD(T)/aCVQZ level of theory, (HBr)<sub>2</sub> and (HI)<sub>2</sub> have  $D_e$  of 7.59 and 6.52 kJ mol<sup>-1</sup>, respectively. These values decreased slightly to 7.38 and 6.22 kJ mol<sup>-1</sup> when extrapolated to the CBS limit. Interestingly, the  $D_e$  results obtained with the valence-only correlation procedure (aTZ, aQZ and a5Z columns in Table III) are quite similar to those from the corresponding expanded valence treatment (aCVNZ columns), differing by approximately 0.1 kJ mol<sup>-1</sup> for (HBr)<sub>2</sub> and 0.4 kJ mol<sup>-1</sup> for (HI)<sub>2</sub> when  $N = Q$  or 5. When comparing the last two columns of Table III, the CBS  $D_e$  values obtained here are within *ca.* 0.2 kJ mol<sup>-1</sup> of other CCSD(T) benchmark data reported in the literature for (HF)<sub>2</sub>, (HCl)<sub>2</sub> and (HBr)<sub>2</sub>.<sup>61,62</sup> The difference grows to more than 1 kJ mol<sup>-1</sup> for (HI)<sub>2</sub>, but that is because the CP procedure utilized to construct the CCSD(T)/aTZ potential energy surface<sup>59</sup> decreases the  $D_e$  by approximately 1.5 kJ mol<sup>-1</sup>.

The shifts in the harmonic vibrational frequencies of the fragments upon complexation are also reported for both hydrogen bond acceptor and donor ( $\Delta\omega(\text{HX})$  and  $\Delta\omega(\text{HY})$ , respectively). Among the data collected for the four homogeneous hydrogen halide dimers in Table IV, the most pronounced donor shift is observed in (HF)<sub>2</sub>, where the computed CCSD(T)  $\Delta\omega(\text{HX})$  values range from -116 to -121 with the aTZ and aQZ basis sets respectively. In a manner consistent with  $D_e$ , the magnitude of the donor frequency shift consistently decreases down the halogen group to *ca.* -50 cm<sup>-1</sup> for (HCl)<sub>2</sub>, -40 cm<sup>-1</sup> for (HBr)<sub>2</sub> and -30 cm<sup>-1</sup> for (HI)<sub>2</sub>.

Although the CCSD(T) computations completed with the aQZ basis set give frequency shifts ( $\Delta\omega$ ) for (HBr)<sub>2</sub> and (HI)<sub>2</sub> that are nearly identical to those obtained with the aCVQZ basis set and the expanded valence-electron correlation including (n-1)*d* electrons, the harmonic stretching frequency values ( $\omega$ ) differ by more than 13 cm<sup>-1</sup>. These results suggest that computations utilizing large aNZ basis sets with conventional valence-electron correlation can reliably predict the stretching frequency shifts, whereas an expanded valence-electron correlation treatment with the aCVNZ basis sets may be required to obtain high-accuracy frequencies for HBr and HI stretches.

## B. Heterogeneous HX/HY Global Minima

Although a number of investigations have carefully compared the two different acceptor...donor configurations of the lightest heterodimer in the hydrogen halide series (i.e. HF...HCl vs. HCl...HF),<sup>38,63-65,67,76,77</sup> very few studies have analyzed both arrangements for systems containing HBr and/or HI. Early analyses employing an electrostatic model and the self-consistent

field (SCF) Hartree-Fock method identified an energetic trend favoring the heavier halogen in the hydrogen bond acceptor position for this heterogeneous series,<sup>68,69</sup> but to the best of our knowledge, there has never been a systematic extension of that work with correlated methods. After probing both acceptor···donor configurations with the MP2 and CCSD(T) methods, we find the same trends for all 6 heterodimers. In the global minimum structure for each heterogeneous pair, the fragment donating the hydrogen bond (HY) always contains the lighter halogen. In other words, HF is always the donor (HY) in the global minimum when forming a hydrogen bonded dimer with heavier hydrogen halides. Similarly, HI is consistently the hydrogen bond acceptor (HX) in the global minimum structure when paired with HF, HCl and HBr.

The bond lengths in all 6 heterogeneous dimer global minima are reported in the middle section of Table I. As noted earlier for the homogeneous (HX)<sub>2</sub> minima, the expanded valence treatment with the aCVQZ basis set produced noticeably shorter bond lengths compared to the conventional valence electron scheme with the aQZ basis set, and the differences could be as large as *ca.* 0.020 Å for R(H-X) and R(H-Y) and up to *ca.* 0.030 Å for R(X···H). However, the two procedures yield nearly identical predictions for the elongation of the monomer covalent bonds upon complexation for both the acceptor and donor ( $\Delta R(\text{H-X})$  and  $\Delta R(\text{H-Y})$ ). The bond length changes are slightly larger for the latter, with the aQZ and aCVQZ  $\Delta R(\text{H-Y})$  values in the middle of Table II growing as large as 0.004 Å in the 3 HF donor minima, 0.009 Å for the 2 HCl donor minima, and 0.013 Å for the lone HBr donor minimum.

The CCSD(T) dissociation energies ( $D_e$ ) for each heterodimer global minima are provided in the bottom half of Table III. The strongest hydrogen bond was observed in HCl···HF and with a  $D_e$  of 12.23 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit, which is only *ca.* 0.1 kJ mol<sup>-1</sup> smaller than the CCSD(T)  $D_e$  reported in reference 72. The hydrogen bond strength decreases by *ca.* 1 kJ mol<sup>-1</sup> in HBr···HF and 2 kJ mol<sup>-1</sup> in HI···HF when HF donates a hydrogen bond to a heavier hydrogen halide, giving  $D_e$  of 11.35 and 10.01 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit, both of which are *ca.* 0.5 kJ mol<sup>-1</sup> smaller than the CCSD(T) results in references 61 and 62.

Compared with the minima featuring HF as the donor, much weaker interactions were observed when HCl donates a hydrogen bond to HBr or HI (by *ca.* 3 kJ mol<sup>-1</sup>). The  $D_e$  values for HBr···HCl and HI···HCl are 8.15 and 7.71 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit. Both are *ca.* 0.1 kJ mol<sup>-1</sup> smaller than the CCSD(T) results reported in References 61 and 62. The weakest hydrogen bond among all six heterodimer global minima was observed in HI···HBr with a  $D_e$  of 7.22 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit. This hydrogen bond is slightly weaker than the one

in (HBr)<sub>2</sub> yet noticeably larger than in (HI)<sub>2</sub> when compared to the homogeneous dimer  $D_e$  data in the upper section of Table III.

By the comparing the  $D_e$  for the ten global minima reported herein, each hydrogen halide's capability of donating a hydrogen bond could be accessed. For the four minima with HI as the acceptor, the  $D_e$  values decrease as the donor contains a heavier halogen, showing the trend  $\text{HI}\cdots\text{HF} > \text{HI}\cdots\text{HCl} > \text{HI}\cdots\text{HBr} > \text{HI}\cdots\text{HI}$ . Because the same  $D_e$  trend was also observed in the three global minima with HBr as the acceptor ( $\text{HBr}\cdots\text{HF} > \text{HBr}\cdots\text{HCl} > \text{HBr}\cdots\text{HBr}$ ) and the two global minima with HCl as the acceptor ( $\text{HCl}\cdots\text{HF} > \text{HCl}\cdots\text{HCl}$ ), the hydrogen bond donating ability decreases from HF down in the halogen group:  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ . Alternatively, a similar analysis of the  $D_e$  data can be used to rank the hydrogen bond accepting ability of the fragments, which increases from HF down in the halogen group:  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ .

The harmonic stretching frequency shifts computed for the six heterodimer global minima are reported in Table IV. The most prominent donor shifts are observed in pairs featuring HF as the donor with  $\Delta\omega(\text{HY})$  values of  $-115$ ,  $-120$  and  $-124\text{ cm}^{-1}$  in  $\text{HCl}\cdots\text{HF}$ ,  $\text{HBr}\cdots\text{HF}$  and  $\text{HI}\cdots\text{HF}$ , respectively, near the CCSD(T) CBS limit. In contrast, the  $\Delta\omega(\text{HY})$  values decrease dramatically when HCl replaces HF as the donor, to *ca.*  $-61$  and  $-70\text{ cm}^{-1}$  in  $\text{HBr}\cdots\text{HCl}$  and  $\text{HI}\cdots\text{HCl}$ .  $\text{HI}\cdots\text{HBr}$  has the lowest  $\Delta\omega(\text{HY})$  of *ca.*  $-55\text{ cm}^{-1}$  for any of the six heterogeneous global minima. Unlike these donor frequency shifts, the decreasing trend observed in  $\Delta\omega(\text{HX})$  for the six heterodimer minima was much less precipitous. Near the CCSD(T) CBS limit, the  $\Delta\omega(\text{HX})$  in  $\text{HCl}\cdots\text{HF}$ ,  $\text{HBr}\cdots\text{HF}$  and  $\text{HI}\cdots\text{HF}$  are  $-18$ ,  $-12$  and  $-5\text{ cm}^{-1}$ , respectively. When HCl or HBr become the donor,  $\Delta\omega(\text{HX})$  is only  $-9$  for  $\text{HBr}\cdots\text{HCl}$  and  $-4\text{ cm}^{-1}$  for  $\text{HI}\cdots\text{HCl}$  and  $\text{HI}\cdots\text{HBr}$ . The trends observed in both the  $\Delta\omega(\text{HX})$  and  $\Delta\omega(\text{HY})$  are consistent with the aforementioned relative hydrogen bond donating abilities of the fragments.

When comparing the frequency results reported in Table IV for the heterodimer global minima using the aNZ and the aCVNZ basis sets, the trend observed is similar to the one in (HX)<sub>2</sub>. Although the computational procedures associated with the large aQZ and aCVQZ basis sets provided similar predictions for the frequency shifts ( $\Delta\omega$ ), the two different computational protocols give harmonic stretching frequencies ( $\omega$ ) for the heterodimers containing at least one HBr or HI fragment that differ by as much as *ca.*  $19\text{ cm}^{-1}$ .

### C. Heterogeneous HX/HY local minima

In addition to the six heterodimer global minima, the corresponding local minima in which the donor and acceptor are exchanged were also systematically investigated in this study along with the planar transition state connecting each pair of minima. In contrast to the hydrogen bond orientation observed in the global minima, all local minima feature the heavier hydrogen halide as the donor and the lighter hydrogen halide as the acceptor. The same bond lengths and changes therein are reported in the bottom sections of Tables I and II, respectively. For the donors, the  $\Delta R(\text{H-Y})$  values are around 0.009, 0.012, 0.014 Å for HCl, HBr and HI, respectively. On the other hand, the  $\Delta R(\text{H-X})$  values for the acceptor fragments were only 0.006 for HCl and 0.008 Å for HBr, whereas no noticeable bond elongation was observed for HF when it accepts a hydrogen bond ( $\Delta R(\text{H-X}) < 0.001$  Å).

The CCSD(T) energy of each local minimum and the transition state relative to the corresponding global minimum ( $\Delta E$  and  $\Delta E^*$ , respectively) are reported in Table V. The HF/HCl, HCl/HBr and HBr/HI systems have the smallest  $\Delta E$  values that range from *ca.* 0.9 to 1.5 kJ mol<sup>-1</sup>. This energy change associated with exchanging the hydrogen bond donor and acceptor increases by roughly 1 kJ mol<sup>-1</sup> for both the HF/HBr and HCl/HI pairs, whereas HF/HI has the largest energy difference with  $\Delta E$  exceeding 3.5 kJ mol<sup>-1</sup>. The barrier heights for the exchange process generally follow the same trend. However,  $\Delta E^*$  is noticeably larger for HF/HCl than HCl/HBr and HBr/HI (by more than a factor of 2) even though they have similar  $\Delta E$  values.

The region of the potential energy surface near the local minimum can be sensitive to the basis set for some of these dimers. For example, the aTZ and aCVTZ  $\Delta E$  and  $\Delta E^*$  values in Table V tend to be somewhat larger than the aQZ and aCVQZ data. The difference is typically less than 0.5 kJ mol<sup>-1</sup>, but it exceeds 1 kJ mol<sup>-1</sup> for the HF/HI dimer. In two cases, the basis set effects were significant enough to change the potential energy surface qualitatively and affect the existence of the local minimum. Although the HCl...HI and HBr...HI local minima were readily identified with the CCSD(T) method when paired with the aTZ and aCVTZ basis sets, neither could be located with the aCVQZ basis set. To help understand this inconsistency, we performed relaxed scans along the in-plane pathway for donor/acceptor exchange. As can be seen from data presented in Figure 1, the barrier for in-plane hydrogen bond donor/acceptor exchange in these dimers vanishes when large quadruple- $\zeta$  basis sets are utilized.

#### D. MP2 computations

In addition to the CCSD(T) computations discussed above, all stationary points reported herein were also thoroughly characterized using the MP2 method with the a*NZ* and a*CVNZ* basis sets. When comparing with the CCSD(T) results, the MP2 computations provided reasonable geometric parameters for the ten global minima. However, with the a*QZ* and a*CVQZ* basis sets, MP2 significantly overestimated the corresponding CCSD(T)  $D_e$  values by *ca.* 1 kJ mol<sup>-1</sup>, with the deviations growing as large as *ca.* 3 kJ mol<sup>-1</sup> for the pairs that include Br or I. The MP2 computations also overestimated the CCSD(T) stretching frequency shifts for both fragments in all the minima, by up to 26 cm<sup>-1</sup> for  $\Delta\omega(\text{HX})$  and 33 cm<sup>-1</sup> for  $\Delta\omega(\text{HY})$  when utilizing quadruple- $\zeta$  basis sets. The MP2 geometrical parameters, harmonic vibrational frequencies and dissociation energies can be found in the Supplementary Material.

#### IV. CONCLUSIONS

Utilizing *ab initio* MP2 and CCSD(T) methods in conjunction with triple- and quadruple- $\zeta$  polarized correlation-consistent basis sets augmented with diffuse functions, this work conducts a comprehensive investigation on the hydrogen halide dimers. Using both the conventional valence electron correlation procedure as well as an expanded valence-electron treatment that includes the (n-1)*d* electrons in Br and I, the global minima of 4 homodimer and 6 heterodimer were thoroughly characterized. The strongest hydrogen bond was computed for HF $\cdots$ HF with a  $D_e$  of 19.11 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit, and these  $D_e$  values for the homogeneous (HX)<sub>2</sub> series decrease down the periodic table to 8.32, 7.38 and 6.22 kJ mol<sup>-1</sup> for HCl $\cdots$ HCl, HBr $\cdots$ HBr and HI $\cdots$ HI, respectively.

The global minimum configurations of the heterogeneous hydrogen halide dimers consistently adopt a specific orientation with the heavier halogen atom always accepting a hydrogen bond from the fragment with the lighter halogen. Thus, HF is always the hydrogen bond donor, whereas HI is consistently the hydrogen bond acceptor. The strongest hydrogen bonds in these heterogeneous dimers were observed in minima featuring HF as the donor, and the  $D_e$  of HCl $\cdots$ HF, HBr $\cdots$ HF and HI $\cdots$ HF are 12.23, 11.35 and 10.01 kJ mol<sup>-1</sup> near the CCSD(T) CBS limit. In contrast, the  $D_e$  of HBr $\cdots$ HCl and HI $\cdots$ HCl are 8.15 and 7.71 kJ mol<sup>-1</sup>, respectively. The weakest hydrogen bond in these 6 heterogeneous systems was observed in HI $\cdots$ HBr with a CCSD(T)  $D_e$  of 7.22 kJ

mol<sup>-1</sup> near the CBS limit.

The hydrogen bonds in the global minima were also characterized by the CCSD(T) harmonic vibrational frequencies. The most pronounced donor shifts computed with quadruple- $\zeta$  basis sets ( $\Delta\omega(\text{HY})$ ) were observed in global minima with HF as the donor with values of *ca.*  $-130\text{ cm}^{-1}$ . The  $\Delta\omega(\text{HY})$  decreased to a range between *ca.*  $-61$  and  $-70\text{ cm}^{-1}$  with HCl as the donor, and *ca.*  $-55$  and  $-32\text{ cm}^{-1}$  in global minima featuring HBr and HI as the donor. A similar yet less prominent trend was observed in the acceptor shifts ( $\Delta\omega(\text{HX})$ ). The  $\Delta\omega(\text{HX})$  values were larger in pairs featuring HF as the donor with magnitudes of *ca.*  $-18$ ,  $-12$  and  $-5\text{ cm}^{-1}$  in HCl $\cdots$ HF, HBr $\cdots$ HF and HI $\cdots$ HF, respectively. The  $\Delta\omega(\text{HX})$  decreased to  $-9$  and  $-4\text{ cm}^{-1}$  in HBr $\cdots$ HCl and HI $\cdots$ HCl when HCl donates a hydrogen bond, and was as low as  $-4\text{ cm}^{-1}$  in HI $\cdots$ HBr and HI $\cdots$ HI near the CCSD(T) CBS limit. Collectively, these results support the established ranking for hydrogen bond donating ability that decreases down the halogen group in the periodic table: HF > HCl > HBr > HI.

In general, there were only small difference between the results obtained with the conventional and expanded valence treatments associated with the aNZ and aCVNZ basis sets, respectively. However, the CCSD(T) aQZ and aCVQZ harmonic stretching frequencies ( $\omega$ ) for the HBr and HI in reported minima deviated by as much as *ca.*  $19\text{ cm}^{-1}$ , which could be significant in subsequent efforts (e.g., anharmonic analyses) to make direct comparisons to experimentally observed vibrational frequencies.

This work also characterized the local minimum and the in-plane TS connecting the two donor/acceptor configurations for each heterogeneous HX/HY pair. However, the HCl $\cdots$ HI and HBr $\cdots$ HI local minima do not exist at certain levels of theory because the CCSD(T) barrier for in-plane hydrogen bond donor/acceptor exchange becomes vanishingly small as the basis set size increases.

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## DECLARATION OF COMPETING INTEREST

The authors have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## DATA AVAILABILITY STATEMENT

The data that support the findings in this research are available in the Supplementary Material or from the corresponding author upon request.

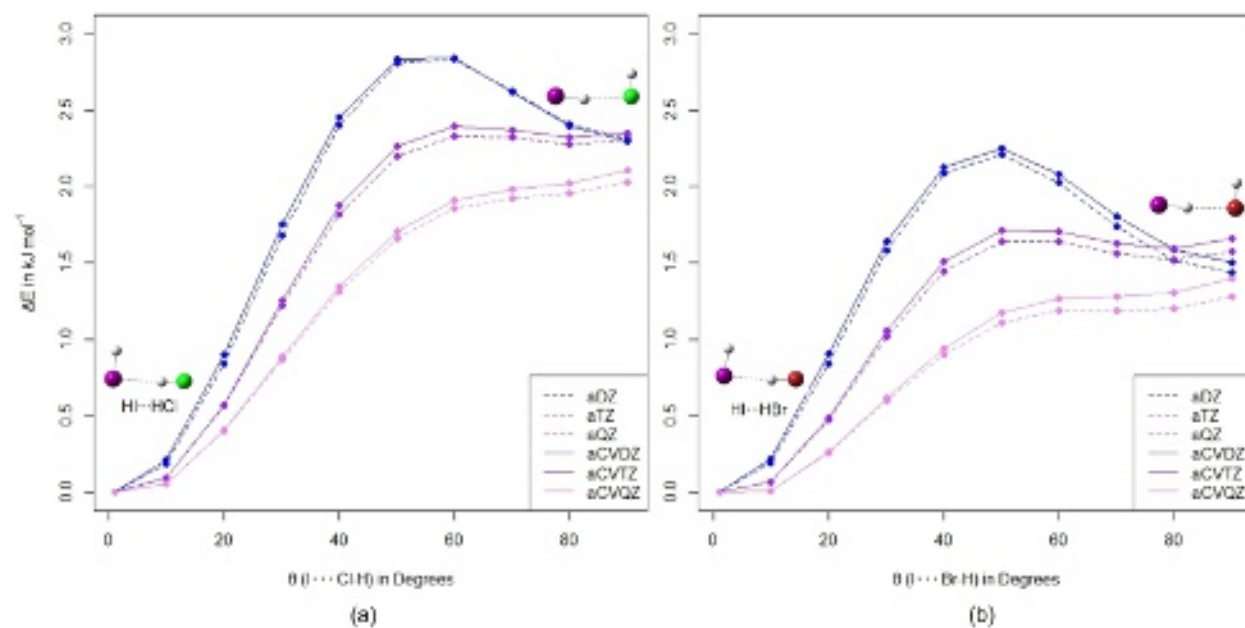


FIG. 1. Relaxed scans of (a) the  $\theta(I \cdots Cl-H)$  bond angle connecting the two different hydrogen bonding configurations of the HCl/Hi dimer and (b) the  $\theta(I \cdots Br-H)$  bond angle connecting the two different hydrogen bonding configurations of the HBr/Hi dimer from constrained CCSD(T) optimizations with various aCVNZ and aNZ basis sets where  $N = D, T$  and  $Q$ .

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TABLE I. Select intra- and inter-fragment bond lengths ( $R$  in Å) of the CCSD(T) optimized global minimum configurations of the homogeneous and heterogeneous hydrogen-bonded dimers  $HX \cdots HY$

$HX \cdots HY$	$R(H-X)$				$R(X \cdots H)$				$R(H-Y)$			
	aTZ	aCVTZ	aQZ	aCVQZ	aTZ	aCVTZ	aQZ	aCVQZ	aTZ	aCVTZ	aQZ	aCVQZ
Homogeneous dimer global minima												
HF $\cdots$ HF	0.924	n/a	0.921	n/a	1.825	n/a	1.818	n/a	0.927	n/a	0.924	n/a
HCl $\cdots$ HCl	1.278	n/a	1.278	n/a	2.531	n/a	2.542	n/a	1.280	n/a	1.280	n/a
HBr $\cdots$ HBr	1.421	1.414	1.420	1.414	2.717	2.705	2.732	2.717	1.423	1.416	1.423	1.416
HI $\cdots$ HI	1.621	1.606	1.619	1.606	3.000	2.967	3.041	3.005	1.623	1.608	1.621	1.609
Heterogeneous dimer global minima												
HCl $\cdots$ HF	1.279	n/a	1.279	n/a	2.311	n/a	2.319	n/a	0.926	n/a	0.923	n/a
HBr $\cdots$ HF	1.421	1.414	1.421	1.414	2.461	2.452	2.470	2.461	0.926	0.926	0.923	0.923
HI $\cdots$ HF	1.621	1.606	1.619	1.606	2.670	2.652	2.679	2.679	0.927	0.927	0.923	0.923
HBr $\cdots$ HCl	1.421	1.414	1.420	1.414	2.662	2.653	2.673	2.663	1.281	1.281	1.281	1.281
HI $\cdots$ HCl	1.621	1.606	1.619	1.606	2.859	2.837	2.886	2.861	1.281	1.282	1.281	1.281
HI $\cdots$ HBr	1.621	1.606	1.619	1.606	2.896	2.868	2.927	2.896	1.424	1.417	1.423	1.417
Heterogeneous dimer local minima												
HF $\cdots$ HCl	0.923	n/a	0.920	n/a	2.068	n/a	2.055	n/a	1.280	n/a	1.281	n/a
HF $\cdots$ HBr	0.923	0.923	0.919	0.919	2.150	2.147	2.142	2.137	1.422	1.415	1.422	1.416
HF $\cdots$ HI	0.922	0.922	0.919	0.919	2.279	2.274	2.284	2.274	1.621	1.606	1.619	1.607
HCl $\cdots$ HBr	1.278	1.278	1.278	1.278	2.601	2.597	1.615	2.609	1.423	1.416	1.422	1.416
HCl $\cdots$ HI <sup>a</sup>	1.278	1.277	-	-	2.730	2.723	-	-	1.622	1.607	-	-
HBr $\cdots$ HI <sup>a</sup>	1.421	1.413	1.420	-	2.835	2.821	2.879	-	1.622	1.697	1.620	-

<sup>a</sup> A local minimum does not exist with certain basis sets. See text for details.

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TABLE II. Covalent bond elongation observed in the hydrogen bond donor and acceptor ( $\Delta R(\text{H-X})$  and  $\Delta R(\text{H-Y})$ , respectively, in Å) in each CCSD(T) characterized minimum

	$\Delta R(\text{H-X})$				$\Delta R(\text{H-Y})$			
	aTZ	aCVTZ	aQZ	aCVQZ	aTZ	aCVTZ	aQZ	aCVQZ
homogeneous (HX) <sub>2</sub> global minima								
HF...HF	0.002	n/a	0.002	n/a	0.005	n/a	0.005	n/a
HCl...HCl	0.006	n/a	0.006	n/a	0.008	n/a	0.008	n/a
HBr...HBr	0.008	0.010	0.008	0.010	0.010	0.012	0.011	0.012
HI...HI	0.011	0.013	0.011	0.013	0.013	0.015	0.013	0.016
heterogeneous HX/HY global minima								
HCl...HF	0.007	n/a	0.007	n/a	0.004	n/a	0.004	n/a
HBr...HF	0.008	0.010	0.009	0.010	0.004	0.004	0.004	0.004
HI...HF	0.011	0.013	0.011	0.013	0.005	0.005	0.004	0.004
HBr...HCl	0.008	0.010	0.008	0.010	0.009	0.009	0.009	0.009
HI...HCl	0.011	0.013	0.011	0.013	0.009	0.010	0.009	0.009
HI...HBr	0.011	0.013	0.011	0.013	0.011	0.013	0.011	0.013
heterogeneous HX/HY local minima								
HF...HCl	0.001	n/a	0.001	n/a	0.008	n/a	0.009	n/a
HF...HBr	0.001	0.001	0.000	0.000	0.009	0.011	0.010	0.012
HF...HI	0.000	0.000	0.000	0.000	0.011	0.013	0.011	0.014
HCl...HBr	0.006	0.006	0.006	0.006	0.010	0.012	0.010	0.012
HCl...HI <sup>a</sup>	0.006	0.005	-	-	0.012	0.014	-	-
HBr...HI <sup>a</sup>	0.008	0.009	0.008	-	0.012	0.014	0.012	-

<sup>a</sup> A local minimum does not exist with certain basis sets. See text for details.

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TABLE III. CCSD(T) dissociation energies ( $D_e$ , in  $\text{kJ mol}^{-1}$ ) for the four homogeneous and six heterogeneous global minima

Minimum	aTZ	aCVTZ	aQZ	aCVQZ	a5Z	aCV5Z	CBS	Lit
homogeneous (HX) <sub>2</sub> global minima								
HF...HF	20.20	n/a	19.77	n/a	19.47	n/a	19.11	19.3 <sup>a</sup>
HCl...HCl	9.00	n/a	8.56	n/a	8.44	n/a	8.32	8.2 <sup>a</sup>
HBr...HBr	7.87	7.95	7.52	7.59	7.37	7.48	7.38	7.6 <sup>a</sup>
HI...HI	6.64	6.98	6.14	6.52	6.04	6.37	6.22	5.1 <sup>b</sup>
heterogeneous HX/HY global minima								
HCl...HF	13.72	n/a	12.86	n/a	12.62	n/a	12.23	12.3 <sup>c</sup>
HBr...HF	12.96	13.00	12.00	12.05	11.71	11.76	11.35	11.8 <sup>a</sup>
HI...HF	12.18	12.41	10.74	10.99	10.41	10.59	10.01	10.5 <sup>a</sup>
HBr...HCl	8.78	8.74	8.37	8.40	8.23	8.27	8.15	8.2 <sup>a</sup>
HI...HCl	8.54	8.74	7.89	8.13	7.74	7.92	7.71	7.8 <sup>a</sup>
HI...HBr	7.93	8.19	7.32	7.61	7.16	7.42	7.22	-

<sup>a</sup> Reference 61,62.

<sup>b</sup> Reference 59.

<sup>c</sup> Reference 72.

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 TABLE IV. CCSD(T) harmonic vibrational frequencies of the hydrogen bond donor and acceptor ( $\omega(\text{HX})$  and  $\omega(\text{HY})$  in  $\text{cm}^{-1}$ ) along with the corresponding frequency shifts relative to the isolated monomer ( $\Delta\omega(\text{HX})$  and  $\Delta\omega(\text{HY})$  in  $\text{cm}^{-1}$  and listed in parentheses) for the four homogeneous and six heterogeneous global minima

Minimum	$\omega(\text{HX})$				$\omega(\text{HY})$			
	$(\Delta\omega(\text{HX}))$				$(\Delta\omega(\text{HY}))$			
	aTZ	aCVTZ	aQZ	aCVQZ	aTZ	aCVTZ	aQZ	aCVQZ
homogeneous $(\text{HX})_2$ global minima								
HF...HF	4088	n/a	4103	n/a	4009	n/a	4021	n/a
	(-37)	n/a	(-39)	n/a	(-116)	n/a	(-121)	n/a
HCl...HCl	2984	n/a	2983	n/a	2947	n/a	2944	n/a
	(-12)	n/a	(-13)	n/a	(-49)	n/a	(-52)	n/a
HBr...HBr	2637	2653	2638	2652	2603	2619	2604	2617
	(-8)	(-8)	(-8)	(-8)	(-41)	(-42)	(-42)	(-43)
HI...HI	2309	2326	2312	2330	2279	2296	2286	2302
	(-4)	(-4)	(-4)	(-4)	(-34)	(-34)	(-30)	(-32)
heterogeneous HX/HY global minima								
HCl...HF	2979	n/a	2977	n/a	4011	n/a	4027	n/a
	(-18)	n/a	(-18)	n/a	(-114)	n/a	(-115)	n/a
HBr...HF	2634	2649	2635	2649	4005	4005	4022	4022
	(-11)	(-11)	(-11)	(-12)	(-120)	(-120)	(-120)	(-120)
HI...HF	2308	2325	2311	2330	3997	3996	4020	4018
	(-5)	(-5)	(-5)	(-5)	(-128)	(-129)	(-122)	(-124)
HBr...HCl	2636	2652	2638	2651	2937	2937	2935	2935
	(-8)	(-9)	(-9)	(-9)	(-59)	(-59)	(-61)	(-61)
HI...HCl	2308	2325	2312	2330	2925	2924	2927	2925
	(-4)	(-5)	(-4)	(-4)	(-71)	(-72)	(-69)	(-70)
HI...HBr	2308	2325	2312	2330	2590	2604	2594	2605
	(-4)	(-5)	(-4)	(-4)	(-55)	(-57)	(-53)	(-55)

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TABLE V. The CCSD(T) relative energies ( $\Delta E$ , in  $\text{kJ mol}^{-1}$ ) of the six heterodimer local minima and the associated electronic energy barriers ( $\Delta E^*$ , in  $\text{kJ mol}^{-1}$ ) for donor/acceptor exchange.

Local minimum	$\Delta E$				$\Delta E^*$			
	aTZ	aCVTZ	aQZ	aCVQZ	aTZ	aCVTZ	aQZ	aCVQZ
HF...HCl	1.42	n/a	0.92	n/a	3.31	n/a	2.68	n/a
HF...HBr	2.75	2.73	2.20	2.16	3.82	3.79	3.14	3.10
HF...HI	4.61	4.71	3.57	3.65	5.03	5.13	3.94	4.01
HCl...HBr	0.91	0.82	0.88	0.85	1.49	1.40	1.15	1.12
HCl...HI <sup>a</sup>	2.29	2.33	–	–	2.35	2.41	–	–
HBr...HI <sup>a</sup>	1.54	1.61	1.21	–	1.67	1.75	1.22	–

<sup>a</sup> A local minimum does not exist with certain basis sets. See text for details.

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