A SAPT Study of the $H_2O \cdots X_2$ Complexes;
X = H, N and F

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Abstract—**The interaction energy of the $H_2O \cdots X_2$ complexes, with X = H, N and F has been analyzed by using the SAPT (Symmetry Adapted Perturbation Theory) methodology. The decomposition of the interaction energy into distinct physical components is a unique feature of SAPT which distinguishes this method from the supermolecular approach. In SAPT, the interaction energy is expressed as a sum of perturbative corrections, each correction resulting from different physical effect. SAPT results show that the above systems possess quite different features; while the complex with hydrogen is dominated by dispersion, a subtle balance of dispersion and induction is effective in stabilizing the complex $H_2O \cdots N_2$, and induction (due to the strong electronegativity of fluorine) is the leading term in the pre-reactive vdW complex $H_2O \cdots F_2$.**

Index Terms—**Symmetry Adapted Perturbation Theory; Potential Energy Surface; van der Waals complexes**

I. Introduction

The nature of intermolecular interactions of water molecules with atoms, such as rare gases, or nonpolar molecules, such as homonuclear diatomics, has been the subject of a wide series of works, both theoretical and experimental. [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12]. Theoretical works were mainly focused on the development of potential energy surface (PES) or relate to accurate calculations of interaction energy using the supermolecular approach. While a few articles discuss the origin of the interaction, results are scattered here and there and no systematic comparative study has been carried out for H_2O–X_2 complexes, at least to the best of our knowledge. This work is aimed at filling the extant gap. The nature of H_2O–X_2 vdW complexes is elucidated by a complete analysis of the single components contributing to the interaction energy.

The paper is organized as follows. In Section II we present the SAPT theory. In Section III results are presented and discussed. Conclusions follow in Section IV.

II. A short overview of SAPT theory

SAPT is designed to calculate the interaction energy of a dimer, i.e. a system consisting of two monomers. In SAPT, the interaction energy is expressed as a sum of perturbative corrections, each correction resulting from a different physical effect. This decomposition of the interaction energy into distinct physical components is a unique feature of SAPT which distinguishes this method from the supermolecular approach, which only holds the total interaction energy. The SAPT

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methodology and its applications are discussed in several review papers. [13], [14], [15], [16], [17]

In SAPT, the total Hamiltonian for the dimer is partitioned as $H = F + V + W$, where $F = F_A + F_B$ is the sum of the Fock operators for monomers A and B, V is the intermolecular interaction operator, and $W = W_A + W_B$ is the sum of the Møller-Plesset operators. The interaction energy, E_{int}, is expanded as a perturbative series

$$E_{\text{int}} = \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} (E_{\text{pol}}^{(nj)} + E_{\text{exch}}^{(nj)}) \tag{1}$$

with the indices n and j denoting the orders in the operators V and W, respectively. The polarization energies $E_{\text{pol}}^{(nj)}$ are identical to the corrections obtained in a regular Rayleigh-Schrödinger perturbation theory. The exchange corrections $E_{\text{exch}}^{(nj)}$ arise from the use of a global antisymmetrizer to force the correct permutation symmetry of the dimer wave function in each order, hence the name "symmetry adaptation".

Omitting the j index, at second perturbative order in V:

$$\begin{aligned} E_{\text{int}} &= E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} \\ &+ E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \Delta E_{\text{int}}, \end{aligned} \tag{2}$$

where ΔE_{int} takes into account the corrections due to third and higher perturbative orders in V, $E_{\text{elst}}^{(1)}$ is the electrostatic energy, $E_{\text{exch}}^{(1)}$ is the exchange energy, $E_{\text{ind(disp)}}^{(2)}$ and $E_{\text{exch-ind(disp)}}^{(2)}$ are the induction (dispersion) energy and its exchange counterpart, respectively.

In the highest currently implemented SAPT:

$$E_{\text{elst}}^{(1)} = E_{\text{elst}}^{(10)} + E_{\text{elst,resp}}^{(12)} + E_{\text{elst,resp}}^{(13)} \tag{3}$$

here the j index has been reintroduced to show that the electrostatic energy is available at the MP3 level; the subscript "resp" means that the coupled Hartree-Fock response of the perturbed system is incorporated in the calculation. This correction takes into account the relaxation of the orbitals of the monomers which occurs in the formation of the dimer, so that it intro-

duces further electron correlation.

The exchange energy is evaluated at the CCSD level:

$$E_{\text{exch}}^{(1)} = E_{\text{exch}}^{(10)} + \varepsilon_{\text{exch}}^{(1)}(\text{CCSD}) \tag{4}$$

The induction energy is corrected for the electron correlation up to second order:

$$E_{\text{ind}}^{(2)} = E_{\text{ind,resp}}^{(20)} + {}^t E_{\text{ind}}^{(22)} \tag{5}$$

${}^t E_{\text{ind}}^{(22)}$ is the MP2 correlation part of $E_{\text{ind}}^{(22)}$ not included in $E_{\text{ind,resp}}^{(20)}$, while for its exchange counterpart:

$$E_{\text{exch-ind}}^{(2)} = E_{\text{exch-ind}}^{(20)} + {}^t E_{\text{exch-ind}}^{(22)} \tag{6}$$

${}^t E_{\text{exch-ind}}^{(22)}$, the exchange counterpart of ${}^t E_{\text{ind}}^{(22)}$, is not effectively computed, but is estimated as:

$$^t E_{\text{exch-ind}}^{(22)} \approx E_{\text{exch-ind,resp}}^{(20)} \frac{{}^t E_{\text{ind}}^{(22)}}{E_{\text{ind,resp}}^{(20)}}. \tag{7}$$

Dispersion energy is available at the MP2 level of correlation:

$$E_{\text{disp}}^{(2)} = E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}, \tag{8}$$

while at the moment its exchange counterpart is only available at the HF level:[1]

$$E_{\text{exch-disp}}^{(2)} = E_{\text{exch-disp}}^{(20)} \tag{9}$$

In the so-called hybrid approach a correction for the induction is introduced:

$$\begin{aligned} \Delta E_{\text{int}} &= \delta E_{\text{int,resp}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - \Big(E_{\text{elst}}^{(10)} \\ &+ E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} \Big). \end{aligned} \tag{10}$$

Considering third-order available components of interaction energy also, the correction for induction is:

[1]Note that the HF level in the operator V is a good approximation, because that operator allows the migration of the electrons of monomer A into the orbitals of B, independently of the nature of the electron denisty (HF, MP2, DFT, etc.). Therefore a SAPT/HF computation includes both exchange and dispersion effects, the last lacking in an ordinary supermolecular HF computation.

$$\delta^3 E_{\text{int}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - \left(E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} \right. \quad (11)$$
$$\left. + \quad E_{\text{ind}}^{(30)} + E_{\text{exch-ind,resp}}^{(20)} + E_{\text{exch-ind}}^{(30)} \right).$$

In fact it can be shown that an appropriate sum of the zeroth order polarization and exchange corrections in V provides a good approximation to the supermolecular Hartree-Fock CP corrected interaction energy, $E_{\text{int}}^{\text{HF}}$ and therefore $\delta E_{\text{int,resp}}^{\text{HF}}$ and $\delta^3 E_{\text{int}}^{\text{HF}}$ represent a good estimate of the higher-order induction and exchange-induction terms.[18]

Overall the accuracy of SAPT is approximately equivalent to the supermolecular MP theory through fourth order, therefore it constitutes a well suited method to treat vdW complexes.[13]

III. $H_2O \cdots X_2$ COMPLEXES

Geometries of the $H_2O \cdots X_2$ complexes $(X = H, N, F)$ have been were optimized using the Gaussian code [19] at the MP2(full)/aug-cc-pVTZ level. Accurate CCSD(T)/aXZ[2] interaction energies were obtained by single point computations carried out by using the Molpro software[20] and the results interpreted by using the SAPT methodology. All the computations included the counterpoise correction (CP) to basis set superposition error (BSSE) and all the elctrons, included core ones, were explicitly correlated. Several local minima were found for all the complexes considered, but we will limit our discussion to the global minimum configurations.

Figure 1 shows the optimized geometries of the free monomers and optimized vdW complexes.

Equilibrium geometries of the *in situ* monomers are very similar to those of the unperturbed monomers because of the interaction between H_2O and X_2 is very weak.

In the vdW complex with hydrogen, the oxygan atom of H_2O acts as the proton acceptor of a very weak hydrogen bond; this in turn causes a slight elongation of the H–H bond with respect to the free H_2

[2]aXZ is aug-cc-pVXZ (X = D, T, Q) abbreviated.

molecule; a very small increase of the $\angle$HOH angle is also observed.

In the H_2O–N_2 complex, on the contrary, water acts as the proton donor, therefore the O–H bond more involved in the interaction is slightly longer than the other; no appreciable variation is found for the N–N bond length. Finally the $H_2O \cdots F_2$ complex is characterized by a F–OH$_2$ halogen bond. The geometry of the water molecule is nearly indistinguishable from that of the free monomer, while just a slight elongation of the F–F distance affects the *in situ* fluorine molecule.
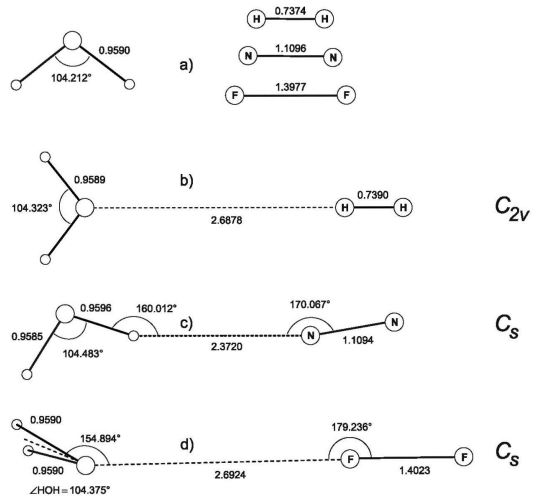

Fig. 1. Optimized (MP2(full)/aTZ, CP included) geometries of the free monomers, a); $H_2O \cdots H_2$, b); $H_2O \cdots N_2$, c); and $H_2O \cdots F_2$, d). Lengths are expressed in Å, angles in degrees.

Overall the geometries of the free monomers predicted by MP2 computations are in excellent agreement with those observed by rotational spectroscopy.[21]

Harmonic frequencies and electrical properties are given in Table I.

The latter ones are very important for vdW complexes beacuse they allow the determination of the interaction energy by means of well-known empirical relationships. [27], [28], [29], [30].

Supermolecular CCSD(T) interaction energies of Table II show that the aDZ basis set is not adequate to describe H_2O–X_2 vdW complexes, while the aTZ+

TABLE I
COMPUTED (MP2(FULL)/ATZ) HARMONIC FREQUENCIES (ω_i, CM^{-1}) AND ELECTRICAL PROPERTIES (DIPOLE MOMENT, μ AND ISOTROPIC POLARIZABILITY, α IN A.U.) OF THE FREE MONOMERS.

	μ	α	ω_1	ω_2	ω_3
H$_2$O	0.732	9.56	1624.85	3845.55	3965.98
	0.7298[22]	9.642[23]	1594.59[24]	3656.65[24]	3755.79[24]
H$_2$	–	5.18	4517.66	–	–
	–	5.3104 [23]	4401[25]	–	–
N$_2$	–	11.62	2220.66	–	–
	–	11.54, 11.367[23]	2359.0[25]	–	–
F$_2$	–	7.81	1009.37	–	–
	–	8.381±0.007[26]	917.00[?]	–	–

TABLE II
INTERACTION ENERGIES (CM^{-1}, CP CORRECTED) OF H$_2$O$\cdots$X$_2$ WITH X = H, N, F EVALUATED AT THE CCSD(T) LEVEL BY USING DIFFERENT BASIS SETS. ALL THE ELECTRONS WERE EXPLICITLY CORRELATED.

	H$_2$O$\cdots$H$_2$	H$_2$O$\cdots$N$_2$	H$_2$O$\cdots$F$_2$
aDZ	−170.02	−346.14	−360.99
aDZ+	−206.67	−410.13	−418.07
aTZ	−209.76	−401.19	−383.58
aTZ+	−214.62	−414.08	−404.40
aQZ	−216.57	−417.75	−401.37
aQZ+	−218.41	−419.01	−408.21
Reference	−235.2[d]	−387.91[k1], −409.61[k2]	−443.0[b]
	−221.2[e]	−441[l]	−511.5[f]
	−255.1[i]	−388.2[a]	
	−235.1[g1], −235.9[g2]	−416.9[i]	
	−236.2[j]		

[a]at MP2/aug-cc-pVDZ [31], [b]at MP2/aug-cc-pVDZ [32], [d]at average of the nine-dimensional fit over the ground vibrational wave function [33], [e]at CCSD(T)-R12 [33], [f]at MP2/aug-cc-pVTZ [34], [g1]at CCCSD(T)-R12 5D PES fit, [g2]at CCCSD(T)-R12 9D PES fit, [7], [i]at MP2/[14s8p/10s] [35], [j]at CCSD(T)/CBS [36], [k1]at MP2/[5s3p2d/3s2p], [k2]at MP2/[7s6p3d/6s3p] [a]The symbol '+' means that additional basis functions were placed in the mid-bond region. The same $(3s\,2p\,1d)$ mid-bond basis set has been used in all the computations. Orbital exponents $s = 0.553, 0.251, 0.117$; $p = 0.392, 0.142$, and $d = 0.328$ are taken from ref [37].

basis yields results close enough to the most accurate aQZ+ ones, at least for a discussion of the most relevant effects. From Table II, it also results quite obvious that the role of mid-bond functions (MBF) becomes less important as the basis set gets larger. In principle a super-molecular approach does not require extra functions to get reliable interaction energies; MBF were added to compare CCSD(T) and SAPT where, on the opposite, MBF are crucial to fully take into account dispersion effects.[37] It is finally to be remarked that for H$_2$O$\cdots$F$_2$ a basis still larger than aQZ+ is needed to achieve the full convergence.

We have investigated the effects of the basis set on the total SAPT interaction energy also, taking the CCSD(T) energies as reference values. We have tested the aDZ, aTZ and aQZ basis sets and all the computations have been carried out in the DC(+)BS approach, the + symbol meaning that additional basis functions have been placed in the midbond region, more specifically in the midpoint of the line joining the centers of mass of the interacting monomers.

Table III, IV and V show the results for the H$_2$O$\cdots$H$_2$, H$_2$O$\cdots$N$_2$ and H$_2$O$\cdots$F$_2$ complexes, respectively. As already observed for CCSD(T), the aDZ+ basis set is not the best one for this study, some convergence can be observed going to aTZ+ to aQZ+. Table VI summarize the SAPT contributions of the interaction energies obtained by using the most extended basis set (aQZ+).

A. H$_2$O$\cdots$H$_2$ *complex*

In the global minimum configuration, the H$_2$O$\cdots$H$_2$ complex is dominated by dispersion

TABLE III
SAPT ENERGY CONTRIBUTIONS (CM^{-1}) FOR THE $H_2O \cdots H_2$, AT DIFFERENT BASIS SET.

contribution	aDZ	aTZ	aQZ
E_{int}^{HF}	-78.2772	-80.1939	-80.6325
$E_{elst}^{(10)}$	-268.2636	-267.4947	-267.5118
$E_{elst,resp}^{(12)}$	15.4295	16.5826	16.2572
$E_{elst,resp}^{(13)}$	4.5069	4.3463	4.056
E_{elst}	-248.3272	-246.5658	-247.1986
$E_{exch}^{(10)}$	259.3969	259.0401	258.6808
$\varepsilon_{exch}^{(1)}(CCSD)$	40.2116	29.1711	25.3808
E_{exch}	299.6085	288.2112	284.0616
$E_{ind,resp}^{(20)}$	-78.9362	-77.2733	-77.2368
$^{t}E_{ind}^{(22)}$	1.4505	2.6988	2.8419
$E_{exch-ind}^{(20)}$	31.14	28.8272	28.7568
$^{t}E_{exch-ind}^{(22)}$	-0.5722	-1.0068	-1.0581
$E_{disp}^{(20)}$	-196.3129	-200.4361	-202.0576
$E_{disp}^{(2)}(k)$	-229.5319	-230.6127	-231.133
$E_{exch-disp}^{(20)}$	21.7953	22.1519	22.5953
$E_{disp}^{(21)}$	-8.9102	-9.207	-9.4203
$E_{disp}^{(22)}$	-24.3088	-20.9697	-19.6551
$E_{[disp]}$	-207.7366	-208.4609	-208.5377
δ_{int}^{HF}	-21.6144	-23.2932	-23.3216
SAPT(2)[a]	-203.3732	-213.5695	-218.3709
SAPT(2)+$\delta_{int,resp}^{HF}$	-224.9876	-236.8627	-241.6925
$E_{ind}^{(30)}$	-61.5813	-66.6692	-66.7075
E_{ind}	-68.5323	-70.0473	-70.0178
$E_{exch-ind}^{(30)}$	57.5784	62.9088	62.9884
$E_{ind-disp}^{(30)}$	-9.6737	-9.7185	-10.0089
$E_{exch-ind-dsp}^{(30)}$	11.8885	12.0265	12.3146
$E_{disp}^{(30)}$	6.7289	7.6842	8.4372
$E_{exch-disp}^{(30)}$	-2.9395	-3.2624	-3.5537
$E^{(30)}$ [b]	2.0013	2.9694	3.4701
$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-4.0029	-3.7604	-3.7191
$\delta 3_{int}^{HF}$	-17.6114	-19.5328	-19.6025
SAPT(2)+$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-207.3761	-217.3299	-222.09
SAPT(3)[c]	-201.3719	-210.6001	-214.9008
SAPT(3)+$\delta^{3}E_{int}^{HF}$	-218.9833	-230.1329	-234.5033
CCSD(T)[d]	-170.0199	-209.7644	-216.5667
CCSD(T)[e]	-206.6663	-214.6229	-218.4051

[a] Defined as $E_{\text{elst,resp}}^{(1)}(3) + E_{\text{exch}}^{(1)}(\text{CCSD}) + E_{\text{ind,resp}}^{(20)} + {}^{t}E_{\text{ind}}^{(22)} + E_{\text{exch-ind,resp}}^{(20)} + {}^{t}E_{\text{exch-ind}}^{(22)} + E_{\text{disp}}^{(2)}(2) + E_{\text{exch-disp}}^{(20)}$.

[b] Defined as $E_{\text{ind}}^{(30)} + E_{\text{exch-ind}}^{(30)} + E_{\text{ind-disp}}^{(30)} + E_{\text{exch-ind-disp}}^{(30)} + E_{\text{disp}}^{(30)} + E_{\text{exch-disp}}^{(30)}$.

[c] Defined as $\text{SAPT(2)} + E^{(30)}$.

[d] Supermolecular calculation.

[e] Supermolecular calculation with additional basis functions placed in the mid-bond region.

TABLE IV
SAPT ENERGY CONTRIBUTIONS (CM^{-1}) FOR THE $H_2O \cdots N_2$, AT DIFFERENT BASIS SET.

contribution	aDZ+	aTZ+	aQZ+
E_{int}^{HF}	-68.8753	-72.7188	-72.4701
$E_{elst}^{(10)}$	-444.1322	-448.4649	-448.4232
$E_{elst,resp}^{(12)}$	-100.1944	-81.4558	-79.2688
$E_{elst,resp}^{(13)}$	42.3525	43.6460	43.7028
E_{elst}	-501.9741	-486.2747	-483.9892
$E_{exch}^{(10)}$	528.6731	527.6007	527.8106
$\varepsilon_{exch}^{(1)}(CCSD)$	108.6645	78.1737	58.7765
E_{exch}	637.3376	605.7744	586.5871
$E_{ind,resp}^{(20)}$	-182.8290	-185.6975	-185.7649
${}^t E_{ind}^{(22)}$	-17.5192	-14.4425	-12.7625
$E_{exch-ind}^{(20)}$	79.4882	83.5681	83.6589
${}^t E_{exch-ind}^{(22)}$	7.6168	6.4995	5.7476
$E_{disp}^{(20)}$	-370.1942	-379.9201	-384.0167
$E_{disp}^{(2)}(k)$	-417.4700	-420.5278	-432.5865
$E_{exch-disp}^{(20)}$	35.3884	36.9030	37.9359
$E_{disp}^{(21)}$	49.1949	49.5966	49.2037
$E_{disp}^{(22)}$	-96.4707	-90.2043	-97.7734
$E_{[disp]}$	-382.0816	-383.6248	-394.6505
δ_{int}^{HF}	-50.0752	-49.7251	-49.7515
SAPT(2)[a]	-359.9613	-374.1975	-401.1736
SAPT(2)+$\delta_{int,resp}^{HF}$	-410.0365	-423.9226	-450.9251
$E_{ind}^{(30)}$	-97.2340	-120.6957	-121.107
E_{ind}	-163.3184	-159.7975	-158.8724
$E_{exch-ind}^{(30)}$	85.5080	110.0741	110.5611
$E_{ind-disp}^{(30)}$	-42.2180	-45.2656	-46.243
$E_{exch-ind-dsp}^{(30)}$	27.4684	29.8443	30.6045
$E_{disp}^{(30)}$	11.5890	13.4434	13.3075
$E_{exch-disp}^{(30)}$	-4.3864	-5.0468	-5.792
$E^{(30)}$ [b]	-19.2730	-17.6463	-18.6689
$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-11.7260	-10.6216	-10.5459
$\delta 3_{int}^{HF}$	-38.3493	-39.1035	-39.2056
SAPT(2)+$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-371.6873	-384.8191	-411.7195
SAPT(3)[c]	-379.2343	-391.8438	-419.8425
SAPT(3)+$\delta^3 E_{int}^{HF}$	-417.5836	-430.9473	-459.0481
CCSD(T)[d]	-346.1355	-401.1860	-417.7493
CCSD(T)[e]	-410.1272	-414.0813	-419.0080

[a] Defined as $E_{elst,resp}^{(1)}(3) + E_{exch}^{(1)}(CCSD) + E_{ind,resp}^{(20)} + {}^t E_{ind}^{(22)} + E_{exch-ind,resp}^{(20)} + {}^t E_{exch-ind}^{(22)} + E_{disp}^{(2)}(2) + E_{exch-disp}^{(20)}$.

[b] Defined as $E_{ind}^{(30)} + E_{exch-ind}^{(30)} + E_{ind-disp}^{(30)} + E_{exch-ind-disp}^{(30)} + E_{disp}^{(30)} + E_{exch-disp}^{(30)}$.

[c] Defined as $SAPT(2) + E^{(30)}$.

[d] Supermolecular calculation.

[e] Supermolecular calculation with additional basis functions placed in the mid-bond region.

TABLE V

SAPT ENERGY CONTRIBUTIONS (CM^{-1}) FOR THE $H_2O \cdots F_2$, AT DIFFERENT BASIS SET.

contribution	aDZ+	aTZ+	aQZ+
E_{int}^{HF}	-41.5586	-5.1770	0.6577
$E_{elst}^{(10)}$	-488.4987	-459.0707	-452.8280
$E_{elst,resp}^{(12)}$	-97.8334	-99.9549	-99.2898
$E_{elst,resp}^{(13)}$	44.2001	51.2355	52.2051
E_{elst}	-542.1320	-507.7901	-499.9127
$E_{exch}^{(10)}$	617.0009	621.0360	620.2798
$\varepsilon_{exch}^{(1)}(CCSD)$	103.8393	71.6633	58.5943
E_{exch}	720.8402	692.6993	678.8741
$E_{ind,resp}^{(20)}$	-297.3280	-321.7646	-321.0221
$^t E_{ind}^{(22)}$	-51.3147	-43.8312	-38.5809
$E_{exch-ind}^{(20)}$	228.6374	254.0838	253.4109
$^t E_{exch-ind}^{(22)}$	39.4596	34.6116	30.4552
$E_{disp}^{(20)}$	-433.8617	-450.8265	-456.1484
$E_{disp}^{(2)}(k)$	-469.6670	-478.8339	-481.1618
$E_{exch-disp}^{(20)}$	50.0887	52.6694	54.0004
$E_{disp}^{(21)}$	50.6313	51.0106	50.2893
$E_{disp}^{(22)}$	-86.4366	-79.0181	-75.3027
$E_{[disp]}$	-419.5783	-426.1646	-427.1614
δ_{int}^{HF}	-101.3702	-99.4615	-99.1828
SAPT(2)$^{[a]}$	-321.4158	-318.1557	-323.9369
SAPT(2)+$\delta_{int,resp}^{HF}$	-422.7860	-417.6172	-423.1197
$E_{ind}^{(30)}$	-397.3650	-523.1096	-524.8108
E_{ind}	-181.9159	-176.3619	-174.9197
$E_{exch-ind}^{(30)}$	392.1991	520.6186	522.7450
$E_{ind-disp}^{(30)}$	-63.0714	-71.2826	-73.4073
$E_{exch-ind-dsp}^{(30)}$	59.4467	66.7601	68.5707
$E_{disp}^{(30)}$	7.3334	9.4411	11.0534
$E_{exch-disp}^{(30)}$	-4.0824	-4.8235	-5.4553
$E^{(30)}$ $^{[b]}$	-5.5396	-2.3959	-1.3043
$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-5.1659	-2.4910	-2.0658
$\delta 3_{int}^{HF}$	-96.2044	-96.9704	-97.1170
SAPT(2)+$E_{ind}^{(30)} + E_{exch-ind}^{(30)}$	-326.5817	-320.6467	-326.0027
SAPT(3)$^{[c]}$	-326.9554	-320.5516	-325.2412
SAPT(3)+$\delta^3 E_{int}^{HF}$	-423.1598	-417.5220	-422.3582
CCSD(T)$^{[d]}$	-360.9879	-383.5786	-401.3687
CCSD(T)$^{[e]}$	-418.0706	-404.4003	-408.2142

[a] Defined as $E_{elst,resp}^{(1)}(3) + E_{exch}^{(1)}(CCSD) + E_{ind,resp}^{(20)} + {}^t E_{ind}^{(22)} + E_{exch-ind,resp}^{(20)} + {}^t E_{exch-ind}^{(22)} + E_{disp}^{(2)}(2) + E_{exch-disp}^{(20)}$.

[b] Defined as $E_{ind}^{(30)} + E_{exch-ind}^{(30)} + E_{ind-disp}^{(30)} + E_{exch-ind-disp}^{(30)} + E_{disp}^{(30)} + E_{exch-disp}^{(30)}$.

[c] Defined as SAPT(2) + $E^{(30)}$.

[d] Supermolecular calculation.

[e] Supermolecular calculation with additional basis functions placed in the mid-bond region.

contributions. It behaves the same way as the $CO \cdots H_2$ and $He \cdots He$ complexes studied by Szalewicz and coworkers in ref [38]. The sum $E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}$ holds a quite consistent part, *ca.* 66%, of the difference $E_{\text{int}}^{\text{HF}} - (E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)})$; considering third order contributions also, the 71% of the HF induction energy is recovered; this clearly means that the $\delta E_{\text{int,resp}}^{\text{HF}}$ contribution is not to be included in the total interaction energy because it mainly contains spurious unphysical effects, like those described in ref [39]. Adding the third order energy to SAPT(2) could in principle yield a more reliable total interaction energy. However the discrepancy between SAPT(3) and CCSD(T), 213 vs 219 cm^{-1}, is higher than the one between SAPT(2) and CCSD(T), 216 vs 219 cm^{-1}. The worsening observed in passing from SAPT(2) to SAPT(3) is probably due to the fact that third order contributions do not include the so called "resp" corrections. In fact, current available SAPT computations do not take into account orbital relaxation effects at the coupled Hartree Fock (CHF) for $E_{\text{ind}}^{(30)}$ and $E_{\text{exch-ind}}^{(30)}$ contributions. These effects could be relevant and could contain that part of the third order induction energy neglected in the present computation.

In a recent work, Belpassi et al [8] analyzed the potential energy surface of of $H_2O \cdots H_2$ obtained by cross section measurements in terms of charge transfer effects. The partition of interaction energy in SAPT does not possess a charge transfer component; the above effect is included in the induction and exchange-induction components, which our analysis reveals to be quite small. It should be noted, however, that in the above mentioned study an empirical potential was used, in which induction is modeled as simple a $\mu(H_2O) \cdot \alpha(H_2)$ product, while in SAPT the complete induction series is taken into account. Therefore the present results are to be considered as an alternative description of the nature of interaction energy.

B. $H_2O \cdots N_2$ *complex*

Studies concerning the vdW complex of water with nitrogen are much less abundant than those with H_2;

nonetheless our results are in reasonable agreement with the ones already published [40]. In going from $H_2O \cdots H_2$ to $H_2O \cdots N_2$, the induction dispersion ratio estimated at the HF level is enhanced (0.48 for N_2 vs 0.42 for H_2). This means that the $\delta E_{\text{int,resp}}^{\text{HF}}$ term contains a relevant part of the induction energy not recovered by the second order SAPT, in addition to the above mentioned unphysical effects; the latter effects, on the contrary, are less important than for $H_2O \cdots H_2$. The agreement between SAPT is excellent (−419.01 cm^{-1} CCSD(T) *vs* −415.36 cm^{-1} for SAPT2 and −419.84 cm^{-1} for SAPT3) especially when the third order perturbative terms are taken into account, see also Table VI. The correction $\delta^3 E_{\text{int}}^{\text{HF}}$ (eq. 12) is also needed. As shown in ref [38], for systems in which induction is predicted to be the leading term, or being the same order as dispersion, the hybrid approach should be the best choice. The need of $\delta E_{\text{int,resp}}^{\text{HF}}$ can therefore be rationalized if one observes that the "resp" counterpart of $E_{\text{ind-resp}}^{(20)}$ recovers just 16 cm^{-1} of induction with respect $E_{\text{ind}}^{(20)}$ at the second SAPT order, suggesting that orbital relaxation effects are not relevant at third order.

C. $H_2O \cdots F_2$ *complex*

The $H_2O \cdots F_2$ system is quite peculiar. In the global minimum configuration there is no weak hydrogen bond, at variance with the complexes of H_2 and N_2, the most relevant interaction involves the fluorine and the oxygen atoms located at ca 2.69 Å. This means that exchange repulsions here largely prevail over attractive electrostatic energy. This originates a repulsive energy at the supermolecular HF level. The induction dispersion ratio is high (0.70) at the HF level; this means that the $\delta E_{\text{int,resp}}^{\text{HF}}$ contribution holds a relevant part of the induction energy. It is interesting to note, however, that induction and exchange-induction contributions cancel each other at a large extent both at second and third order levels thus indicating that the perturbative series of induction is not converged and that the inclusion of $\delta E_{\text{int,resp}}^{\text{HF}}$ (eq. 11) is mandatory to get a physically meaningful interaction energy; indeed, by including $\delta E_{\text{int,resp}}^{\text{HF}}$ in

the total energy, we substitute the not converged induction energy of SAPT with the actual HF induction energy. The agreement between SAPT and CCSD(T) for $H_2O\cdots F_2$ is not as good as those encountered for previous systems. Considering only the HF-resp components at second order of SAPT: electrostatic, induction, dispersion and their exchange counterparts an interaction energy of just 302 cm^{-1} is predicted. It is therefore evident that, as already pointed out for CCSD(T), even for SAPT a basis set larger than aQZ is needed to recover electron correlation and achieve quantitative convergence. Nevertheless, at least at a qualitative level, SAPT results show that the halogen bond between fluorine and water can is largely due to induction, the latter probably involving charge transfer effects as those recently invoked for the $F\cdots O$ halogen bond in the $H_2O\cdots CF_4$ vdW complex.[41]

TABLE VI
TOTAL AND MAIN CONTRIBUTIONS OF THE SAPT INTERACTION ENERGY (CM^{-1}, AQZ+ BASIS SET^a) FOR $H_2O\cdots X_2$ WITH X = H, N, F. CCSD(T) TOTAL INTERACTION ENERGIES (SAME BASIS SET) ARE GIVEN FOR COMPARISON.

	$H_2O\cdots H_2{}^b$	$H_2O\cdots N_2{}^c$	$H_2O\cdots F_2{}^d$
E_{elst}	-267.96	-483.98	-753.26
E_{exch}	$+328.07$	$+586.59$	$+1193.64$
$E_{\text{disp}}{}^e$	-212.56	-419.84	-561.80
E_{ind}	-68.09	-135.31	-301.70
Tot	-220.54	-419.84	-423.12
CCSD(T)	-216.60	-419.01	-408.21

^{a}The symbol '+' means that additional basis functions were placed in the mid-bond region. The same $(3s\,2p\,1d)$ mid-bond basis set has been used in all the computations. Orbital exponents $s = 0.553, 0.251, 0.117;\ p = 0.392, 0.142,$ and $d = 0.328$ are taken from ref [37]. ^{b}From SAPT2. ^{c}From SAPT3, no δE^{HF} correction included. ^{c}From SAPT2, $\delta E^{\text{HF}}_{\text{int,resp}}$ correction included. ^{e}Exchange counterparts have been included both in dispersion and induction energies.

IV. CONCLUSION

The interaction energy of the global minimum configurations of the $H_2O\cdots X_2$ vdW complexes (X = H, N, O) has been computed at the CCSD(T) level and the physically meaningful components of energy are analyzed by using the SAPT methodology. While the complex with hydrogen is largely dominated by dispersion, in $H_2O\cdots N_2$ a subtle balance of dispersion and induction is observed. Finally, the pre-reactive complex $H_2O\cdots F_2$ is largely dominated by induction owing to the strong electronegativity of fluorine.

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