

THEORETICAL STUDY OF H₂...I⁻ VAN DER WAALS ANION COMPLEXMichal ILČIN^{a1}, Vladimír LUKEŠ^{b1}, Viliam LAURINC^{b2,*} and Stanislav BISKUPIČ^{a2}^a Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic; e-mail: ¹ michal.ilcin@stuba.sk, ² stanislav.biskupic@stuba.sk^b Department of Chemical Physics, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic; e-mail: ¹ vladimir.lukes@stuba.sk, ² viliam.laurinc@stuba.sk

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

The *ab initio* potential energy surface (PES) for the weak interaction of hydrogen molecule with iodine anion is presented. The surface was obtained by the supramolecular method at the MP4(SDTQ) level of theory. Our calculations indicate the van der Waals (vdW) system for the linear configuration at $r_{\text{H-H}} = 0.752 \text{ \AA}$ and $R = 3.76 \text{ \AA}$ with a well depth of $D_e = 2096 \mu E_h$. The presented PES reveals also a transition state for the perpendicular arrangement at $r_{\text{H-H}} = 0.7416 \text{ \AA}$ and $R = 4.63 \text{ \AA}$ with an interaction energy of $-113 \mu E_h$. The physical origin of stability of the vdW H₂...I⁻ structure with respect to the H₂...X⁻ (X = F, Cl, Br) one was analysed by the symmetry adapted perturbation theory (SAPT) based on the single determinant HF wave function. The separation of the interaction energy shows that the dispersion forces play a much more important role for the systems with Cl, Br and I than for H₂...F⁻ and their importance slightly increases in the order Cl < Br < I. The global importance of the electrostatic and the induction energies decreases in the order F > Cl > Br > I.

Keywords: Halogen anion complexes; Hydrogen; Iodine anion; van der Waals complex; Interaction energy; Potential energy surface; Intermolecular perturbation theory; SAPT.

During last decade, the van der Waals complexes involving hydrogen molecule and halogen anions have been intensively studied¹⁻⁶. Theoretical and experimental studies demonstrated that the long-range part of PES plays an important role in the reaction dynamics⁷.

In the case of the reaction of F + H₂, the FH₂⁻ photodetachment experiments of Neumark and co-workers^{8,2-4} have shed light on the potential energy surface (PES) in the region of the transition state. The anionic complex of H₂...Cl⁻ has been recently investigated spectroscopically by Bieske and co-workers^{9,10}. Photoelectron spectrum of the H₂...Cl⁻ anion reported by Neumark and co-workers¹¹ is the first experimental proof of the H₂ + Cl prereactive vdW region. The hydrogen–halide weak interaction up to the

Br^- and I^- anions was examined by infrared spectroscopy in very recent papers of Bieske's group^{12,13}.

Based on the spectroscopic studies, the complexes are deduced to possess linear equilibrium structures, with averaged intermolecular separations between the halogen anion and H_2 centre of mass of 3.20 Å ($\text{H}_2\ldots\text{Cl}^-$), 3.46 Å ($\text{H}_2\ldots\text{Br}^-$) and 3.85 Å ($\text{H}_2\ldots\text{I}^-$)¹³. Experimental data clearly support the expectation that the intermolecular bond should become longer and weaker with increasing halide size. The ratios between the dissociation energies are 1:0.8:0.62 for $\text{Cl}:\text{Br}:\text{I}$ anions^{12,13}. The experimental harmonic stretching force constants for the intermolecular bond also vary in the expected way with 2.9, 1.9 and 1.3 N m⁻¹ for $\text{H}_2\ldots\text{Cl}^-$, $\text{H}_2\ldots\text{Br}^-$ and $\text{H}_2\ldots\text{I}^-$, respectively. A small red shift of the H_2 stretching mode reflects the linear vdW bond between H_2 molecule and the halide anion. The binding energies trace the proton affinities in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (ref.¹²).

The theoretical *ab initio* calculation of the $\text{H}_2\text{--Cl}^-$ complex performed by Alexander¹⁴ indicate the position of the minimum for the linear structure at $R = 3.07$ Å in Jacobi co-ordinate system with a well depth of 855.8 cm⁻¹. Recently published three-dimensional PES computed using CCSD(T) method¹⁵ and corrected on the basis set superposition error (BSSE)^{16,17} shows the minimum at $R = 3.09$ Å with a well depth of 835.7 cm⁻¹. In our recent study¹⁸ we presented the *ab initio* PES of $\text{H}_2\ldots\text{Br}^-$ system. In this paper we focus our attention on the next anion complex in the halide series of $\text{H}_2\ldots\text{X}^-$ vdW systems.

Main goals of this work are: (i) to evaluate the BSSE-free PES for the vdW area of the $\text{H}_2\ldots\text{I}^-$ system at the supermolecular MP4(SDTQ) theoretical level; (ii) to provide an analytical form of calculated PES; (iii) to analyse the physical origin of the stability of vdW structure of the calculated system by means of the intermolecular perturbation theory I-PT based on the single determinant HF wave function; (iv) to compare the results for $\text{H}_2\ldots\text{I}^-$ with similar anion systems including all other halogens, namely $\text{H}_2\ldots\text{F}^-$, $\text{H}_2\ldots\text{Cl}^-$, $\text{H}_2\ldots\text{Br}^-$, and with experimental data.

METHODOLOGY AND DEFINITIONS

The *ab initio* methods used for calculations of interaction energies can be classified as supermolecular, perturbational, and hybrid ones¹⁹. The interaction energy in supermolecular approach is obtained as the difference between the value of the energy of the complex E_{AB} and the sum of the energies of its constituents ($E_{\text{A}} + E_{\text{B}}$)

$$\Delta E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} . \quad (1)$$

Interaction energies at different levels of theory are identified by appropriate superscripts, e.g. $\Delta E_{\text{int}}^{\text{MP}n}$ ($\Delta E_{\text{cor}}^{\text{MP}n}$) denotes the interaction (interaction correlation) energy calculated at the n -th order of the Møller-Plesset perturbation level of theory. The total supermolecular interaction energy (ΔE_{int}) is represented by the sum of the HF interaction energy ΔE^{SCF} and relevant interaction correlation energy. It is clear that in the supermolecular approach the interaction energy is obtained as a single number. Its decomposition into terms with clear physical meaning is not straightforward and additional calculations are necessary for a better physical understanding of the interaction^{19,20}.

The perturbational methods compute the interaction energy directly as the sum of distinct physical contributions. For the analysis of the interaction energy the many-body formulations of the symmetry adapted perturbation theory (SAPT)^{21,22} was used. The interaction energy is expressed as the sum

$$E_{\text{int}} = \sum E_{\text{els}}^{(nij)} + \sum E_{\text{ind}}^{(nij)} + \sum E_{\text{disp}}^{(nij)} + \sum E_{\text{exch}}^{(nij)} + \sum E_{\text{other}}^{(nij)} + \dots \quad (2)$$

where E_{elst} is the electrostatic interaction energy, E_{ind} is the induction energy, and E_{disp} is the quantum mechanical dispersion energy. The subscript "exch" expresses the exchange-overlap corrections. The superscript n in Eq. (2) denotes the order of the perturbation V_{AB} and i (j) indicate the order of the Møller-Plesset fluctuation potential for the A (B) system.

To analyse the supermolecular results, the interpretative tools based on the intermolecular perturbation theory (I-PT) are applied at the SCF as well as at the post-HF theoretical levels. The HF-SCF interaction energy is separated as the sum of the Heitler-London (ΔE^{HL}) energy²³ and the HF deformation contribution ($\Delta E_{\text{def}}^{\text{HF}}$).

$$\Delta E^{\text{HF}} = \Delta E^{\text{HL}} + \Delta E_{\text{def}}^{\text{HF}} . \quad (3)$$

The ΔE^{HL} may be further divided into the first-order Hartree-Fock electrostatic $E_{\text{els}}^{(100)}$ (for the notation of this and further perturbation terms, see, e.g., refs^{19,20}) and HL exchange-penetration $\Delta E_{\text{exch}}^{\text{HL}}$ components

$$\Delta E^{\text{HL}} = \Delta E_{\text{exch}}^{\text{HL}} + E_{\text{els}}^{(100)} . \quad (4)$$

The HF deformation energy originates in mutual electric polarisation effects. At the distances where intermolecular overlap is small, this term might be approximated using the sum of the second-order HF Coulomb ($\Delta E_{\text{ind_resp}}^{(200)}$) and the exchange induction ($\Delta E_{\text{exch_ind_resp}}^{(200)}$) energies with response effects (respective subscripts)^{19,22}.

In addition to the above mentioned interaction energy contributions, the second-order MP2 correlation interaction energy can be partitioned as

$$\Delta E_{\text{cor}}^{(2)} = E_{\text{els_resp}}^{(12)} + E_{\text{disp}}^{(200)} + E_{\text{exch_disp}}^{(200)} + \Delta E_{\text{other}}^{(2)} \quad (5)$$

where $E_{\text{els_resp}}^{(12)}$ denotes the second-order electrostatic correlation energy (containing $E_{\text{els_resp}}^{(102)}$ and $E_{\text{els_resp}}^{(120)}$ energies). $E_{\text{disp}}^{(200)}$ and $E_{\text{exch_disp}}^{(200)}$ represent the second-order dispersion and SAPT exchange-dispersion energies²². The remaining term $\Delta E_{\text{other}}^{(2)}$ encompasses the remaining exchange and deformation correlation corrections as well as the response effects.

Using the diagrammatic techniques²⁴⁻²⁶, it is possible to distinguish the third-order interaction energy contributions like the dispersion-correlation ($E_{\text{disp}}^{(210)}$, $E_{\text{disp}}^{(201)}$, $E_{\text{disp}}^{(211)}$, $E_{\text{disp}}^{(202)}$, $E_{\text{disp}}^{(220)}$), third-order dispersion ($E_{\text{disp}}^{(300)}$) and/or mixed induction-dispersion ($E_{\text{ind_disp}}^{(21)}$) energies. However, the complete physical interpretation of the higher than second-order contributions of the interaction electron-correlation energies is not straightforward.

CALCULATION DETAILS

All I-PT calculations were performed using SAPT program²² codes interfaced to the Gaussian 03 program package²⁷. The supermolecular calculations were performed using Gaussian 03 program package and BSSE was determined via the counterpoise method of Boys and Bernardi¹⁶. The presented HF interaction energy terms were developed using dimer-centered basis sets of the constituent monomers. In all supermolecular electron-correlated calculations, a frozen core approximation was used. The importance of the core electrons was tested in the subsequent calculations in which all electrons were correlated. In this case, the energies around the stationary points differ less than 2.5%. The role of core electrons was tested also with respect to the relativistic effect for iodine anion by the Douglas-Kroll^{28,27} method.

The inclusion of core electrons with relativistic corrections leads to more negative interaction energies (2%) with respect to the non-relativistic approach.

For halogen atoms we used the basis set POL reported by Sadlej²⁹ for supermolecular calculations. It represents the near triple- ζ quality basis set augmented by the polarisation functions optimised to reproduce molecular electric properties, especially polarisabilities. Due to computational restrictions and capabilities, the SAPT calculations were performed using 6-311G** basis sets³⁰. The augmented correlation consistent basis sets (aug-cc-pVTZ and aug-cc-pVQZ) of Dunning^{31,32} has been used for the hydrogens.

A system of Jacobi coordinates (r , R , Θ) was used in all our calculations. The coordinates R and Θ represent in turn the distance from halogen atom to the centre of mass of hydrogen molecule, and the Jacobi angle. If this convention is used, $\Theta = 0^\circ$ denotes the linear orientation, while $\Theta = 90^\circ$ designates the T-shaped geometry. The coordinate r stands for H₂ intramolecular distance.

RESULTS AND DISCUSSION

For the sake of comparison, the geometries of stationary points and the interaction energies of all anion complexes were determined. The supermolecular results are collected in Table I. These interaction energies are calculated from Eq. (1) with energies of complex constituents in Eq. (1) calculated with optimised complex geometries. The optimised equilibrium distance of pure hydrogen molecule is 0.7416 Å. In all the investigated complexes, a vdW minimum was found in the linear arrangement. The BSSE correction has a minimal effect on the intramolecular distance r . For H₂...F⁻ complex, the difference between BSSE-uncorrected and -corrected values of r is approximately 0.007 Å, but for H₂...Cl⁻ it is only 0.001 Å. The difference in distance r for the H₂...I⁻ complex is even smaller and can be neglected. The geometry of the potential energy minimum of H₂...I⁻ complex (Table II) calculated including the BSSE correction is in very good agreement with BO-RKR results based on the experimental data ($R = 3.76$ Å)¹³. The result also agrees with BO-RKR data ($R = 3.13$ Å for H₂...Cl⁻¹⁰ and 3.38 Å for H₂...Br⁻¹³). From comparison with the experimental results it is clear that the BSSE correction is essential in order to obtain good results for the used basis set. In the perpendicular orientation of H₂...Cl⁻, the saddle point is localised at $r = 0.7416$ Å and $R = 4.63$ Å. The corresponding interaction energy is $-113 \mu E_h$ (see Table I).

TABLE I

Stationary points on the $H_2...X^-$ ($X = F, Cl, Br, I$) PES with and without the BSSE correction. Supermolecular interaction energy calculated at the MP4/aug-cc-pVTZ+POL level is defined as the difference between the dimer energy and the energies of monomers in the configurations in which they are in the dimer

r, Å	Θ = 0°				Θ = 90°			
	BSSE-uncorrected		BSSE-corrected		BSSE-uncorrected		BSSE-corrected	
	R, Å	$E_{int}, \mu E_h$	R, Å	$E_{int}, \mu E_h$	R, Å	$E_{int}, \mu E_h$	R, Å	$E_{int}, \mu E_h$
$H_2...F^-$	0.7866	2.108	-14383	2.19	-10331	0.7422	2.822	-1255
$H_2...Cl^-$	0.7556	2.887	-5797	3.13	-3628	0.7416	3.641	-642
$H_2...Br^-$	0.7533	3.058	-5035	3.40	-2800	0.7416	3.809	-697
$H_2...I^-$	0.7520	3.245	-5176	3.76	-2096	0.7416	4.020	-891

TABLE II
Equilibrium structures (R values in parenthesis are BSSE-corrected optimal values) and real harmonic vibrational frequencies of the H-H stretch for the systems under study. T = mass center of H₂. Vibrational frequency of isolated H-H molecule is 4433 cm⁻¹

H ₂ ...X	X = F			X = Cl			X = Br			X = I
	stationary point	global minimum	transition state							
r _{H-H} , Å	0.7866	0.7422	0.7556	0.7416	0.7536	0.7416	0.7520	0.7418	0.7418	
R _{X-T} , Å	2.108 (2.19)	2.822 (3.18)	2.887 (3.13)	3.641 (3.98)	3.058 (3.40)	3.809 (4.26)	3.245 (3.76)	4.020 (4.63)	4.020 (4.63)	
α _{X-T-H*} , °	0	90	0	90	0	90	0	90	90	
ω _{H-Hstretch} , cm ⁻¹	3636	4423	4181	4433	4217	4433	4239	4433	4433	

Position of the minimum on the $\text{H}_2\ldots\text{I}^-$ PES was also examined with CCSD(T) approach. The difference in localisation of the minimum using MP4 and CCSD(T) method was very small, approximately 0.02 Å in R (r was held constant). The interaction energy calculated using MP4 method was slightly deeper (1.5%) around the minimum when compared with BSSE-corrected CCSD(T) calculation. Similar results for the convergence of the MP4 method were discussed in our recent work¹⁸ for $\text{H}_2\ldots\text{Cl}^-$ and $\text{H}_2\ldots\text{Br}^-$ systems.

The effect of a halogen anion in the vicinity of the hydrogen molecule on the vibration of the hydrogen molecule can be seen in Table II. The influence on the vibration with the halogen anion in T-configuration is negligible. In the linear arrangement the vibration frequency increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$. Complexes with Cl, Br and I show only moderate changes in the intramonomer frequency while in $\text{H}_2\ldots\text{F}^-$ complex the intramonomer vibration frequency has a very large red shift. The calculated trend of the change of frequencies is in agreement with the experimental observations^{10,13}.

The two-dimensional PES (data are available on request) of the ground electronic state of the $\text{H}_2\ldots\text{I}^-$ vdW complex at $r = 0.752$ Å was calculated in the range of R from 2.9 to 9.0 Å and Θ from 0 to 90°. The obtained potential energy points were fitted to the following general functional form

$$E_{\text{int}}(R, \Theta) = \sum_{L=0}^6 P_L^0(\cos \Theta) \left[\sum_{k=0}^6 a_k^L \left[\exp(-a_1(R - a_2)) \right]^k + \frac{b_1^L}{R^4} + \frac{b_2^L}{R^6} + \frac{b_3^L}{R^8} \right] \quad (6)$$

where $P_L^0(\cos \Theta)$ denotes a Legendre polynomial of order L . The rigorous least-square fitting procedure based on the singular value decomposition was used to determine all 72 variational parameters (Table III). Prior to the least square calculation, the original grid of 150 potential energy points was expanded by the bicubic spline interpolation procedure to 1350 points. After successful fit the covariance matrix was calculated and no significant correlation between parameters was observed. The average absolute deviation of the fit was 0.7 μE_h . The evaluated PES reveals two stationary points (Fig. 1). The potential energy minimum occurs for linear geometry at $R = 3.76$ Å, and its interaction energy amounts to $-2096 \mu\text{E}_h$.

Within the supermolecular calculations, the truncation effect of the correlation treatment on the values of the interaction energies is illustrated in Figs 2a, 2b. As one can see, the interaction energy at HF level, ΔE^{SCF} at the stationary point in the linear arrangement, is attractive. The attractive char-

TABLE III
Parameters of the analytical potential (see Eq. (6)) ($a_1 = 0.36687$, $a_2 = 5.61173$, all parameters are in μE_h)

L	a_0^L	a_1^L	a_2^L	a_3^L	a_4^L	a_5^L	a_6^L	b_1^L	b_2^L	b_3^L
0	94.02373	-399.71568	674.44658	-1359.03806	1048.63908	-511.82248	119.33706	-6.33771	-2.75541	-2.04745
1	-12.23255	-225.55398	61.80166	-311.58823	229.40407	-108.47631	19.23505	-0.98074	0.10084	0.12046
2	14.59179	-93.63783	225.10246	-252.38176	148.50915	-45.46494	5.73250	-2.65436	-1.67820	-1.24117
3	-7.80506	41.83435	-133.83823	146.31663	-84.41361	21.29525	-1.70708	0.02345	-0.19776	-0.11886
4	5.89609	-58.48410	121.65382	-164.11849	104.15310	-34.39553	4.63630	-2.17944	-1.44841	-1.05781
5	18.47030	-112.89038	290.51550	-315.54918	177.72209	-47.46445	4.67899	0.02828	0.54755	0.34936
6	-21.03326	153.42390	-343.85928	396.99488	-228.53223	66.46260	-7.78444	-1.78285	-2.11149	-1.47208

acter of ΔE^{SCF} decreases in the order F > Cl > Br > I. In T-shaped geometry ΔE^{SCF} is repulsive except for the system with fluorine. Repulsive values of ΔE^{SCF} in this geometry increase in the order F < Cl < Br < I. Thus, whereas in the linear arrangement correlation energy only shifts the HF interaction energy to more negative values, for the saddle point in the perpendicular arrangement it is crucial to change the shape of PES from repulsive to attractive. A dominant part of the interaction correlation energy naturally originates from the MP2 level of theory. As can be seen from the correlation energies up the MP n order, $\Delta E_{\text{cor}}^{\text{MP}n}$, in Figs 3a, 3b, the third and fourth levels of the perturbation theory only finely tune the total interaction energy. One exception is $\text{H}_2\ldots\text{F}^-$ in the perpendicular configuration, where $\Delta E_{\text{cor}}^{\text{MP}2}$ shifts negative ΔE^{SCF} to higher values and the higher-order terms are necessary. Correlation interaction energy contributions up to the order n , $\Delta E_{\text{cor}}^{\text{MP}n}$, are comparable within systems containing Cl, Br, I. For the absolute value of $\Delta E_{\text{cor}}^{\text{MP}n}$, the trend for linear arrangement is decreasing in the order Cl > Br > I while for the T-shaped configuration the absolute value of $\Delta E_{\text{cor}}^{\text{MP}n}$ increases in the same order.

The next step of this study is to discuss the physical origin of the stability of the indicated vdW structures. Using the decomposition of the supermolecular MP n interaction energy, we can analyse and estimate the influence of the fundamental components on the interaction energy in the stationary points (in the minimum and the saddle point). These dependences are shown in Figs 2 and 3.

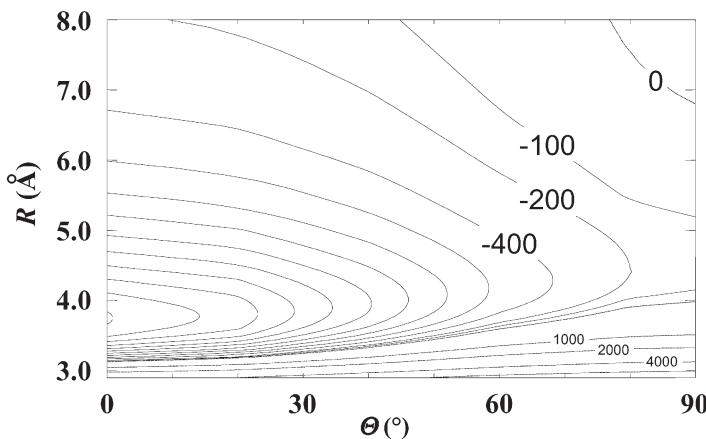


FIG. 1
Contour plot of the PES ($r = 0.752$ Å) calculated at the MBPT4/aug-cc-pVTZ+POL level of theory. The solid (dotted) lines stand for negative (positive) values of the interaction energies

The relevance of electrostatic, induction and dispersion forces can be assessed on the basis of the relations of $\Delta E_{\text{els}}^{(100)}$, $\Delta E_{\text{ind-resp}}^{(200)}$ and $\Delta E_{\text{disp}}^{(200)}$ contributions to the interaction energy. The ratio $\Delta E_{\text{els}}^{(100)} : \Delta E_{\text{ind-resp}}^{(200)}$ for the minimum in the linear configuration is almost constant for all the systems (1.20, 1.23, 1.19, 1.26 in the series F, Cl, Br, I), so the ratio of the electrostatic and the induction attractive forces does not vary considerably within the set of H₂...X⁻ halide complexes. The saddle point in the perpendicular arrangement is destabilized by the repulsive character of the electrostatic energy. The ratio $\Delta E_{\text{els}}^{(100)} : \Delta E_{\text{disp}}^{(200)}$ for the linear configuration (on the ratio $\Delta E_{\text{ind-resp}}^{(200)} : \Delta E_{\text{disp}}^{(200)}$) is 2.36, 1.42, 1.33, 1.08 (2.83, 1.75, 1.58, 1.36) in the sequence from F to I.

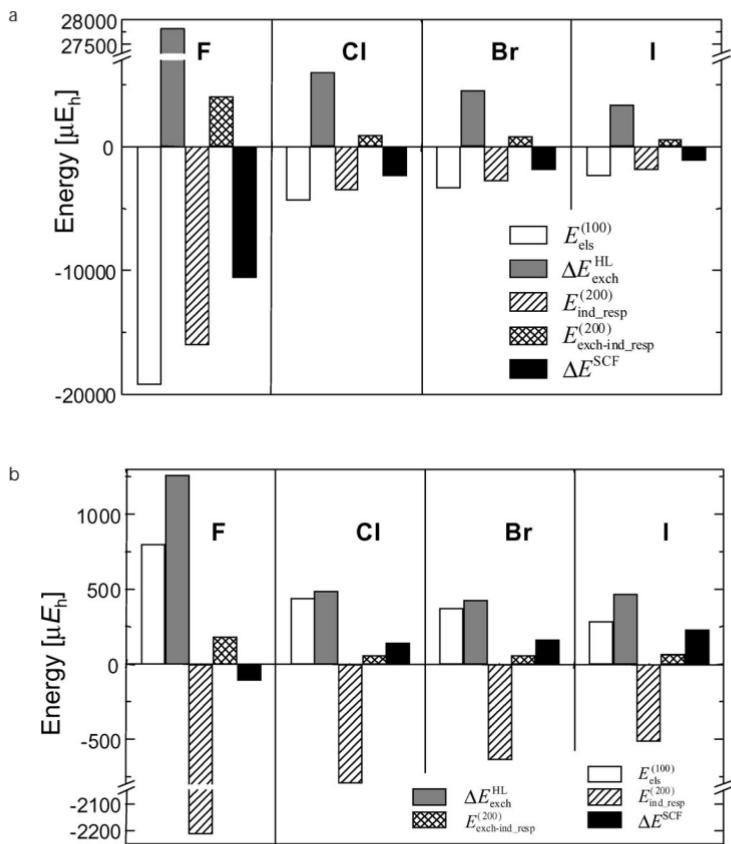


FIG. 2

The dependence of the HF interaction energies and their SAPT components of interacting H₂X⁻ (X = F, Cl, Br, I) in the BSSE-corrected stationary points (see Table I) for: a linear configuration, b perpendicular configuration (calculated in the 6-311G**+aug-cc-pVQZ basis set)

These numbers clearly show the increasing importance of the dispersion energy in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$. The system involving fluorine does not fit into the set of the three other complexes in which the decrease of the ratio is slow, while for fluorine there is a much bigger step in the ratio considered. Similar behaviour can be observed also for the ratio $\Delta E_{\text{ind-resp}}^{(200)} : \Delta E_{\text{disp}}^{(200)}$ in the perpendicular arrangement. The corresponding ratios in the order from F to I are 4.35, 2.63, 2.16 and 1.54.

For heavier atoms the relativistic effects may change the position of the extremal points on the PES^{33,34}. The inclusion of the relativistic effects by the Douglas-Kroll method stabilised the complex in the minimum region

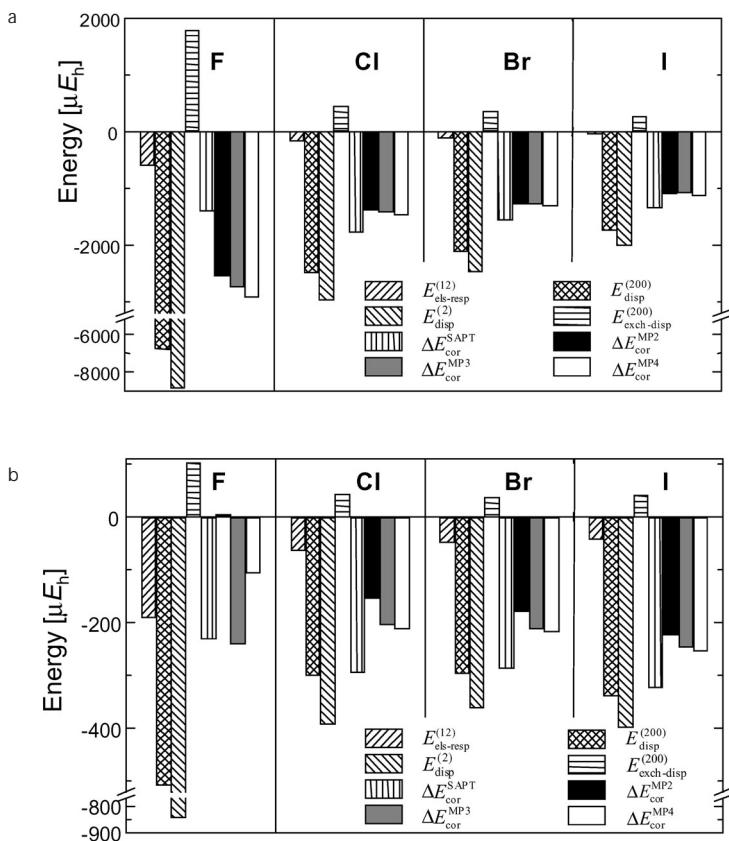


FIG. 3

The dependence of the correlation interaction energies and their SAPT components of interacting H_2X^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) in the BSSE-corrected stationary points (see Table I) for: a linear configuration, b perpendicular configuration (calculated in the 6-311G**+aug-cc-pVQZ basis set)

only about 2%. However, for precise relativistic calculations other types of basis sets must be used.

CONCLUSIONS

The *ab initio* potential energy surface for the H₂...I⁻ interaction was evaluated at the supermolecular MP4 level. The minimum occurs in the linear geometry and the transition state in the perpendicular configuration. The calculated results are in very good agreement with BO-RKR results based on the experimental data^{10,13}. For the sake of comparison, the physical origin of the stability of all anion complexes was analysed using the SAPT method. The interaction energies were separated into four fundamental components – electrostatic, exchange-penetration, induction and dispersion. The separation of the interaction energy shows that the dispersion forces play a much more important role for systems with Cl, Br and I than for H₂...F⁻ and their importance slightly increases in the order Cl < Br < I. The global importance of the electrostatic and the induction interactions decreases in the order F > Cl > Br > I.

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