

# A post-HF study on the interaction of iodine with small polyaromatic hydrocarbons

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**Abstract** In this work, we present a theoretical study of the interaction between a diatomic iodine molecule with planar naphthalene and several other small polyaromatic hydrocarbons (PAHs). Our aim was to understand the general characteristics of the potential energy surface (PES) of this system; that is locating various local minima, finding the variation of PES around these optimum points by means of first principle calculations at MP2, SCS-MP2 and CCSD(T) levels of theory. Two basic orientations of the iodine molecule, i.e., parallel or perpendicular with respect to the naphthalene plane, are discussed. The PES of the former was investigated in detail, including the translation and rotation of I<sub>2</sub> (as a rigid rotor) along the naphthalene surface. It was concluded that, although the perpendicular conformations are usually 1 kcal mol<sup>-1</sup> more stable than the parallel conformation, this small difference does not exclude the presence of both conformations in the gas phase. Both structures were stable enough to hold more than 20 vibrational states. NBO analysis showed that the mutual polarization effects were greater for the perpendicular conformation. It was also observed that the I<sub>2</sub>+naphthalene dimer interaction is almost twice of that of I<sub>2</sub>+naphthalene, showing the long range character of the interaction.

**Keywords** Iodine · Polyaromatic hydrocarbons · Noncovalent interactions · Halogen bonding

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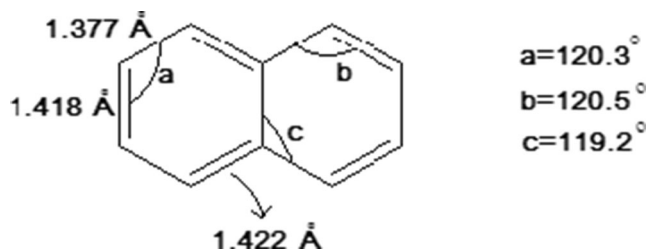
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## Abbreviations

PES	Potential energy surface
COM	Center of mass
MP2	Second order Møller-Plesset perturbation theory
SCS-MP2	Spin component-scaled second order Møller-Plesset perturbation theory
CCSD(T)	Coupled cluster theory including single double and perturbative triple excitations
CP	Counterpoise
DFT	Density functional theory
BSSE	Basis set superposition error

## Introduction

Graphene has attracted a great deal of interest due to its exceptional electronic [1, 2] and mechanical [3] properties. It is a zero bandgap, single layer of graphite, comprised of a two-dimensional network formed by sp<sup>2</sup> hybridized carbon atoms. Since every carbon atom is a surface atom, graphene has a very large surface area, which makes it eligible for single molecule detection and chemical vapor sensing applications. The sensing mechanism of graphenes is similar to that of carbon nanotubes [3] and it based on the charge transfer between the adsorbate (donor) and surface (acceptor) and the change in the mobility of charge carriers. The adsorption of small gas molecules such as H<sub>2</sub>, O<sub>2</sub>, CO, NO, H<sub>2</sub>O, NO<sub>2</sub>, and NH<sub>3</sub> [4–11] onto the surface of carbon nanotubes or graphene has been studied by first-principles calculations using density functional theory (DFT) methods. Such studies have demonstrated drastic



**Fig. 1** Molecular geometry of naphthalene. All C–H bonds lengths are  $1.09 \text{ \AA}$

changes in electrical properties like electrical resistance [12] and conductivity [13]. Although the interaction between the adsorbate molecules and surface atoms is a weak, noncovalent interaction, it plays an important role in the overall properties of these nanomaterials and must be treated with high level quantum mechanical calculations, which are possible only for limited sized graphene-like surfaces. Polyaromatic hydrocarbons (PAHs) can be used as a theoretical model that will enable us to characterize such interactions accurately. For example, ab-initio calculations at the second order of Møller-Plesset perturbation theory (MP2) have been employed to study coronene- $\text{H}_2$  interactions in detail [14] for estimating graphite- $\text{H}_2$  binding energy. The study of adsorption phenomena of diatomic molecules, especially halogen, onto the graphene surface has provided significant insight into charge-transfer induced spectral shifts and has enabled a systematic investigation of varying electron affinities of halogens on the adsorption energy and electronic properties of the surface. Periodic DFT calculations on interaction of the graphene surface with halogen atoms [15] and halogen molecules [16] have been reported. Although diatomic halogen molecules did not cause any surface damage during adsorption, small molecular weight halogen atoms F and Cl changed the hybridization state of carbon atoms from  $sp^2$  to  $sp^3$ . This effect was not observed for Br and I [15]. Among the studied homonuclear diatomic

halogen molecules,  $\text{I}_2$  showed the weakest electron affinity towards the graphene surface as observed in Raman shifts and also in DFT calculations [16].

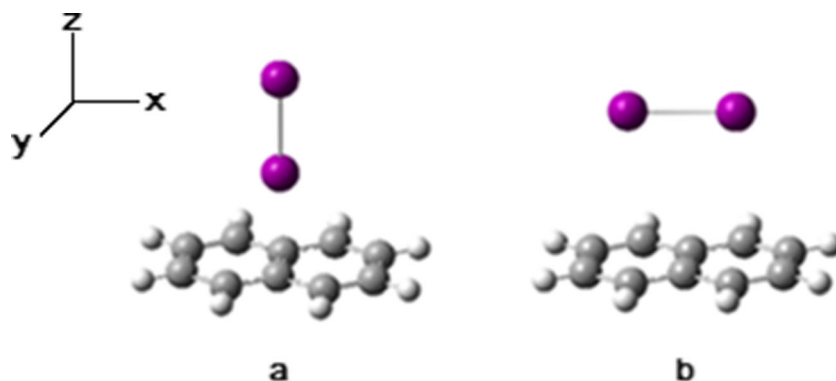
In this work, we chose the  $\text{I}_2$  molecule as an adsorbate molecule with which to calculate the binding energies quantitatively. There are several reasons for this choice of the  $\text{I}_2$  molecule: (1) it is a symmetrical molecule and can be modeled as a rigid rotor; (2) it is known to have a very weak van der Waals (vdW) interaction with nanocarbon surfaces; (3) the power of different ab-initio methods and the DFT method (the most commonly used method in the literature) on quantitative description of weak interactions can be tested. The PAHs chosen were naphthalene, pyrene, tetracene and coronene molecules, consisting of 2, 4, 4 and 6 fused benzene rings, respectively. The most likely binding sites of  $\text{I}_2$  on these surfaces were searched by using several grids in terms of the vertical and horizontal distances between the centers of mass (COMs) of  $\text{I}_2$  and naphthalene as well as an orientational angle. The binding energies, as a function of the adsorbate's orientation with respect to the PAH's molecular plane and distance to the surface, were determined quantitatively via accurate post HF methods, at MP2, spin component-scaled-MP2 (SCS-MP2) and coupled cluster theory including single double and perturbative triple excitations [CCSD(T)] levels of theory.

#### Computational methods

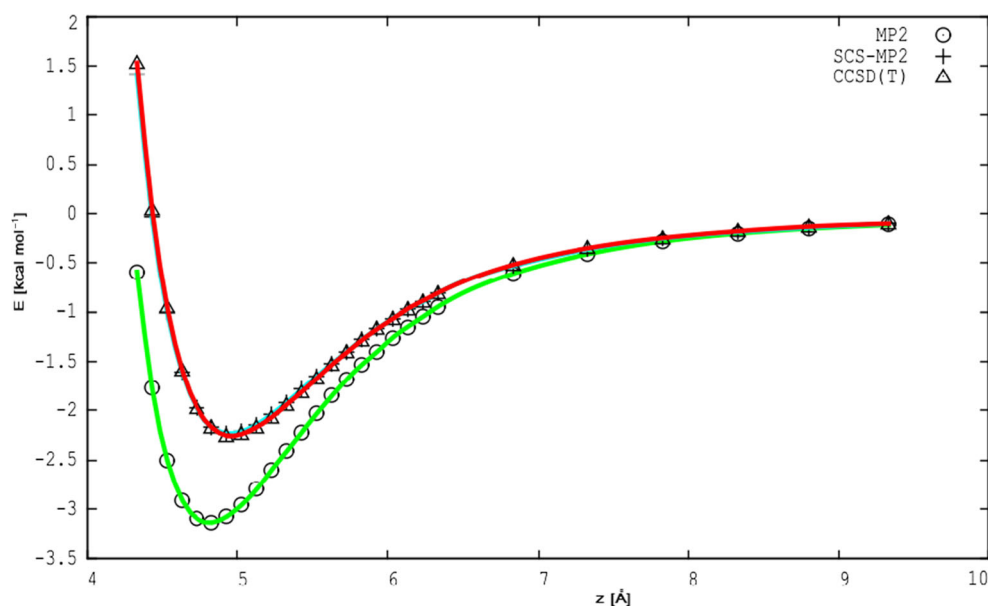
The simplest model compound we chose with which to study  $\text{I}_2$ -PAH interactions was naphthalene. The geometry of naphthalene (Fig. 1), was optimized with aug-cc-pVDZ/MP2 calculations using MOLPRO [17] keeping  $D_{2h}$  symmetry.  $\text{I}_2$  was kept frozen at an equilibrium bond length of  $2.66 \text{ \AA}$  [18].

The interactions between  $\text{I}_2$  and PAHs are similar in nature to interactions between PAHs, i.e., they are classified as non-covalent interactions [19–21], and are long-range and weak. Therefore, simple DFT calculations cannot describe  $\text{I}_2$  bonding to a PAH. Although there are numerous recipes for

**Fig. 2** Iodine–naphthalene system with **a** perpendicular and **b** parallel approach of the iodine towards the surface



**Fig. 3** Potential energy for the perpendicular conformation of the iodine-naphthalene system



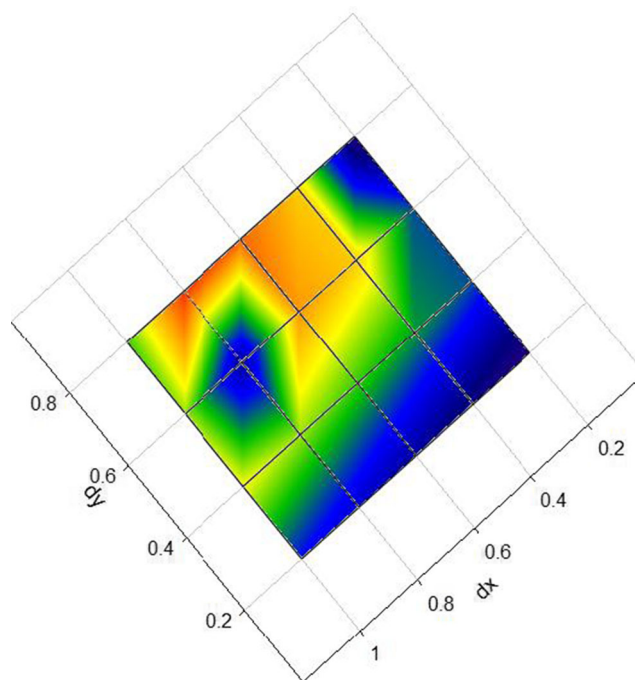
adapting DFT for such long-range interactions, e.g., dispersion corrected DFT [22–24] or symmetry-adapted perturbation theory DFT [25–27], we used ab initio methods where the electron correlation is calculated explicitly. Unfortunately, the most economical MP2 method is known to overestimate such weak interactions and cannot be used reliably. In this work, most calculations were carried out within the coupled-cluster theory where single and double excitations were included explicitly and perturbative triple excitations were added. In order to extend our work to larger systems, we also looked at results of the SCS-MP2 theory [28]. In this approach, the energy of any closed-shell species is a linear combination of the singlet and triplet states. We chose the standard coefficients of 2/3 and 1/3 for singlet and triplet configurations.

The basis sets were chosen such that a large set of calculations could be carried out without compromising the accuracy of the results. For iodine, the ECP-46MWB basis set was employed as implemented in the MOLPRO basis set library [29]. In the conventional notation for ECP $n$ XY,  $n$  is the number of core electrons that are

replaced by the pseudopotential, then X denotes the reference system used for generating this pseudopotential (X = S: single-valence-electron ion; X = M: neutral atom), and Y stands for the theoretical level of the reference data (Y = HF: Hartree-Fock; Y = WB: quasirelativistic; Y = DF: relativistic). With 46 electrons, iodine is left with seven

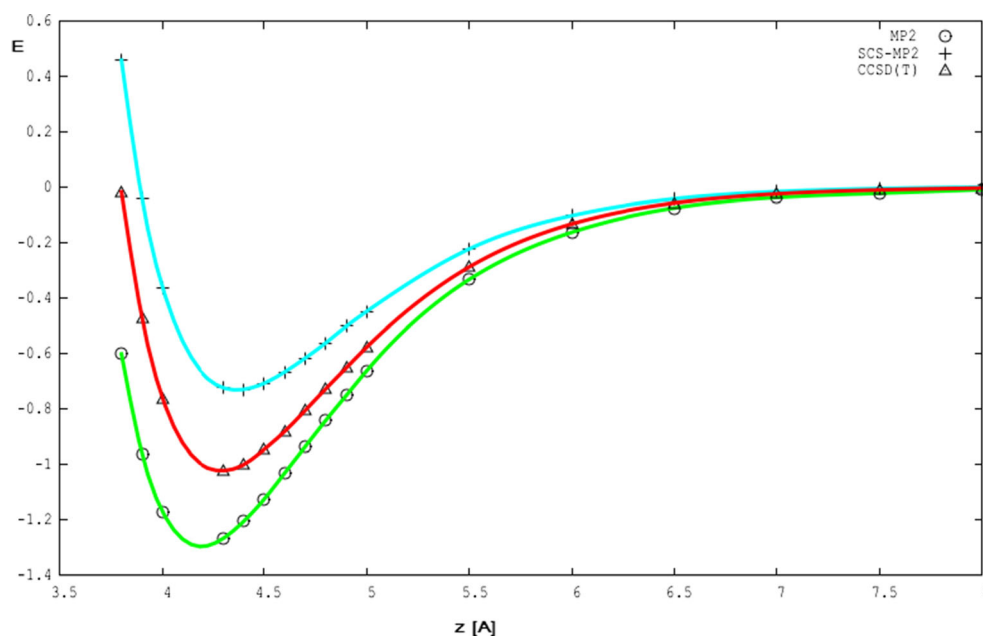
**Table 1** Complete basis set (CBS) limits of the potential energy of the perpendicular conformation of I<sub>2</sub> (in kcal mol<sup>-1</sup>). SCS-MP2 Spin component-scaled second order Møller-Plesset perturbation theory, CCSD(T) coupled cluster theory including single double and perturbative triple excitations

Basis set	E(SCS-MP2)	E(CCSD(T))
aug-cc-pVDZ	-2.19	-2.22
aug-cc-pVTZ	-2.94	-3.10
CBS	-3.26	-3.48



**Fig. 4** Contour diagram of coupled cluster theory including single double and perturbative triple excitations [CCSD(T)] interaction energies with respect to the displacements along the short and long axis of naphthalene. The color scale from red to blue shows increasing interaction energy

**Fig. 5** Potential energy function for the parallel conformation of I<sub>2</sub> (in kcal mol<sup>-1</sup>)



[5 s,5p] valence electrons. The usual choice for post-HF methods is the correlation consistent basis sets. In order to avoid the common problem of linearly dependent basis sets, we opted to use aug-cc-pVDZ for carbon and cc-pVDZ basis for hydrogen. Once the local minima along the potential energy surface (PES) are found, we used aug-cc-pVTZ basis for carbon and cc-pVTZ for hydrogen atoms at these points for single point energy calculations. Utilizing the results of these two calculations, we extrapolated to the complete basis set limit for the interaction energies.

These basis sets are not very large so the basis set superposition error (BSSE) is not negligible. The Boys' counterpoise method was used to correct BSSE for all structures considered.

To study the PES, two orientations of I<sub>2</sub> were considered: I<sub>2</sub> approached to the PAH surface either perpendicularly or parallel to the molecular plane. In the first case (Fig. 2a), I<sub>2</sub> is above the COM of naphthalene and, in the second case (Fig. 2b), it lies parallel to the long axis of naphthalene. Throughout the manuscript, the distance between the I<sub>2</sub> and the COM of the adsorbate molecule is denoted as *z* and varied

**Table 2** CBS limits of the potential energy of the parallel conformation of I<sub>2</sub> (in kcal mol<sup>-1</sup>)

Basis set	E(SCS-MP2)	E(CCSD(T))
Z <sub>c</sub> (Å)	4.4	4.3
aug-cc-pVDZ	-0.72	-1.02
aug-cc-pVTZ	-1.22	-1.60
CBS	-1.43	-1.84

usually by 0.1 Å, which is sufficient to observe the variation in the interaction strength.

To find other global/local minima on the PES and to study how the PES changes around these optimum points, we shifted the I<sub>2</sub> molecule along a grid of the naphthalene surface and rotated when possible.

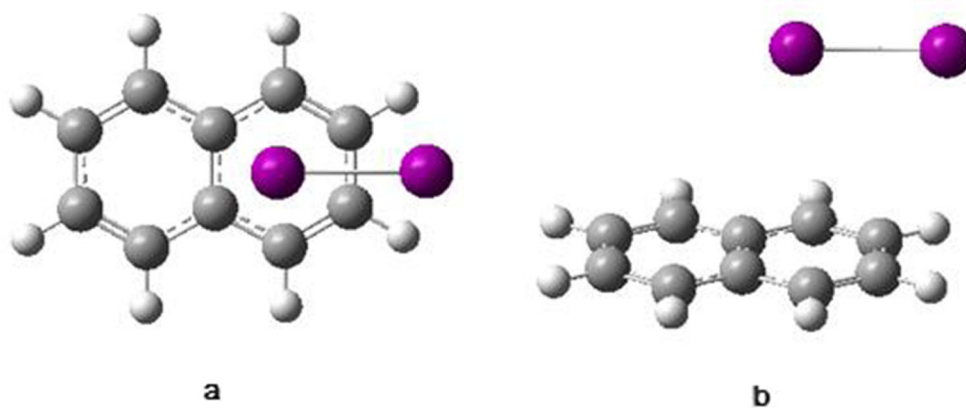
Finally, to understand the possible edge effects [19], we computed the interaction energies between I<sub>2</sub> and tetracene, pyrene and coronene molecules. For these calculations, the SCS-MP2 method was used with the same basis sets with the exception of coronene, where the cc-pVDZ basis set was used for carbons due to the strong linear dependence of the augmented basis set.

## Results and discussion

### Perpendicular conformation

First, we studied the perpendicular conformation as in Fig. 2a. The BSSE-corrected potential energy curves for MP2, SCS-MP2 and CCSD(T) are plotted in Fig. 3. It is a well known fact that MP2 overestimates interaction energies, and this is especially critical for the strengths of non-covalent interactions. The MP2 minimum energy was found at *z*<sub>c</sub>=3.8 Å with the potential depth of *D*<sub>e</sub>=3.10 kcal mol<sup>-1</sup>. The corresponding values for CCSD(T) were found to be *z*<sub>c</sub>=4.7 Å and *D*<sub>e</sub>=2.22 kcal mol<sup>-1</sup>. For this potential energy curve, SCS-MP2 seemed to work very well, resulting in *z*<sub>c</sub>=4.7 Å and *D*<sub>e</sub>=2.19 kcal mol<sup>-1</sup>. On the other hand, CCSD calculations without the triple excitations underestimated the interactions,

**Fig. 6a,b** The geometry of the global minimum structure of in-plane configuration. **a** Bird's-eye view, **b** side view



resulting in too shallow a potential well with  $z_e=4.8 \text{ \AA}$  and  $D_e=1.85 \text{ kcal mol}^{-1}$ .

Lacking the necessary three body contributions to dispersion, induction and induction-dispersion interactions and also the fourth order dispersion interaction, CCSD fails strongly around the minimum energy conformation. However, all these methods perform reasonably well beyond  $7.0 \text{ \AA}$  region as they include the second order vdW contributions, especially as dipole–quadrupole, quadrupole–quadrupole and dipole–octupole pairwise interactions. In the repulsive region where  $z < 4.2 \text{ \AA}$ , again SCS-MP2 and CCSD(T) gave almost the same slope, with  $V$  going down as  $z^{-24}$ . This exponent was found to be 30 for MP2 and 22 for CCSD.

The calculations were repeated with aug-cc-pVTZ basis sets at the equilibrium bond length obtained from CCSD(T). Then, two extrapolation techniques were used for the Hartree-Fock and correlation energies to obtain the complete basis set

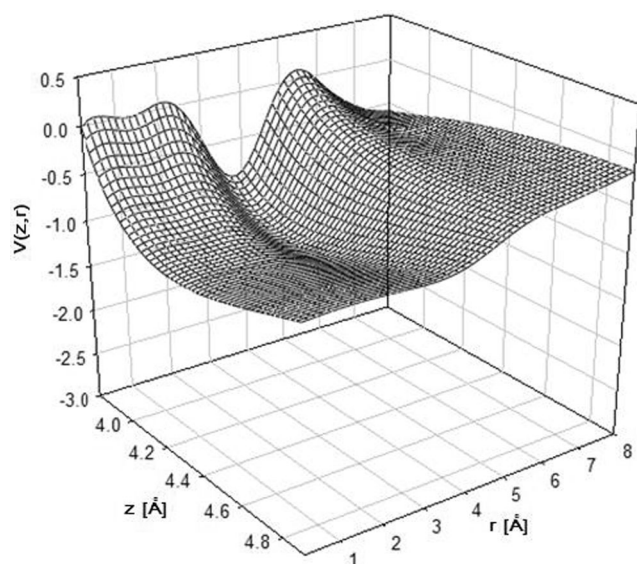
limits for the interaction strengths. The two-point extrapolation formulas are :

$$E(X) = E(\text{CBS}) + A(X+1) \exp(-9sqtr(X)) \quad (1a)$$

$$E(X) = E(\text{CBS}) + AX^{-3} \quad (1b)$$

Equation (1a) was used to extrapolate Hartree-Fock energies and Eq (1b) for the correlation energy. In Table 1, we present the SCS-MP2 and CCSD(T) results.

So far we have found only a local minimum energy conformation of the perpendicular approach of an  $I_2$  molecule. To search for a global minimum, we constructed a grid over the naphthalene molecule with  $0.2 \text{ \AA}$  intervals. Defining the long axis of the naphthalene as the  $x$ -axis, we observed that the global minimum is actually slightly off-center in the  $x$ -direction. This structure at  $\Delta x=0.5$  and  $\Delta y=0.0 \text{ \AA}$  has a slightly larger potential depth of  $D_e=2.23 \text{ kcal mol}^{-1}$ . However, upon carrying out the complete basis set limit extrapolations, we have found out that the global minimum is still at the center of mass of the naphthalene. The complete potential energy surface is plotted as a contour plot in Fig. 4.



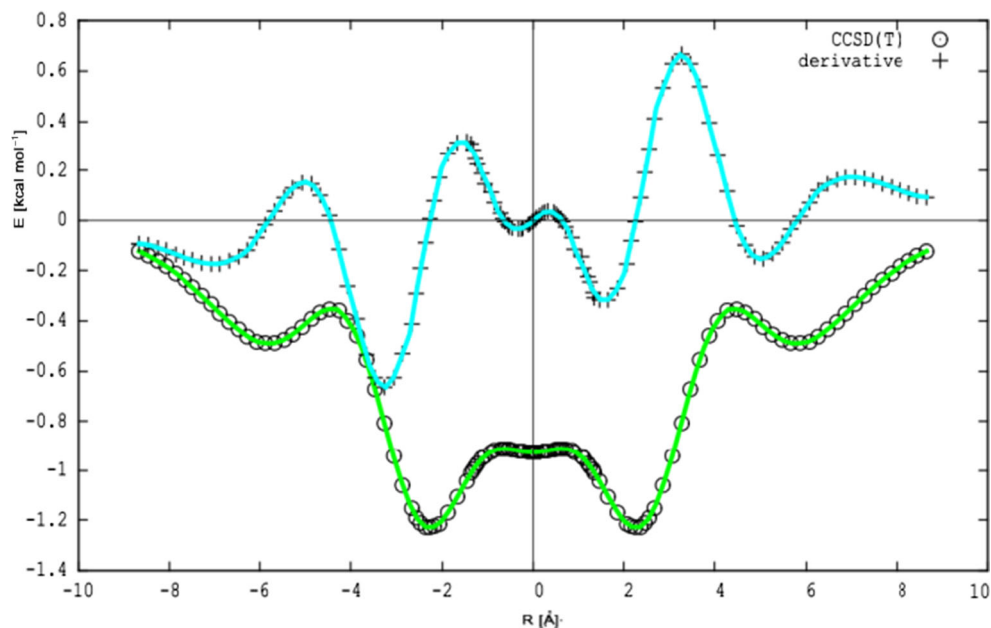
**Fig. 7** Potential energy surface (PES) in terms of  $z$  and  $\Delta x$  (in  $\text{kcal mol}^{-1}$ )

#### Parallel conformation

The parallel conformation of  $I_2$  has three degrees of freedom:  $z$ , the perpendicular distance between the center of masses;  $r$ , in-plane displacement of the center of masses and  $\theta$ , the orientational angle.

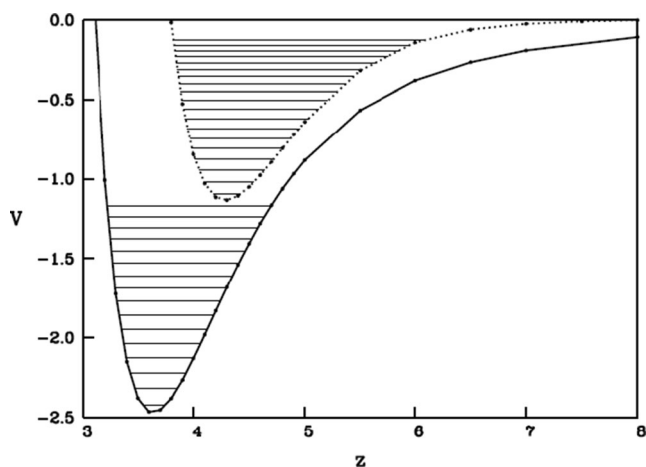
First, we placed  $I_2$  along the long axis of naphthalene, where both COMs were at the origin of the coordinate system ( $r=0, \theta=0$ ) as in Fig. 1b. The potential energy curves for this conformation as a function of the distances between the center of masses are plotted in Fig. 5.

**Fig. 8** Potential energy and friction force as a function of  $\Delta x$  at  $z=4.1$  Å



Potential energy curves show exactly the same trends as in the perpendicular approach, i.e., MP2 overestimates the bonding and CCSD is too repulsive. In this case the difference between SCS-MP2 and CCSD(T) results were relatively larger. In Table 2, we summarize the results.

Using MP2 and CCSD methods, equilibrium bond distances were found to be 4.2 and 4.4 Å, respectively. Potential depths were 2.14 and 1.41 kcal mol<sup>-1</sup> at the CBS limit. We searched the global minimum for the parallel conformation by moving I<sub>2</sub> along both axes of naphthalene while keeping the rotational angle  $\theta=0$ . The variation in the potential energy along the long axis shows a number of variations due to iodine atoms interacting strongly with different carbon atoms. By restricting the  $z$ -coordinate to a set of fixed values between 3.8–7.0 Å, we shifted I<sub>2</sub> until both iodine atoms left the



**Fig. 9** Potential energy curves and the vibrational levels of the perpendicular and parallel approaches of I<sub>2</sub>.  $V$  is in kcal mol<sup>-1</sup> and  $z$  is in Å

boundaries of the naphthalene plane. The minimum energy conformation corresponds to  $z=4.1$  Å and  $\Delta x=2.3$  Å. This structure is depicted in Fig. 6 and the corresponding well depth was 2.11 kcal mol<sup>-1</sup> at the CBS limit. The strength of the interaction was -2.41 kcal mol<sup>-1</sup> for MP2, -1.67 kcal mol<sup>-1</sup> for SCS-MP2 and -1.69 kcal mol<sup>-1</sup> for CCSD.

The 3-dimensional potential energy surface in ( $z$ ,  $\Delta x$ ) coordinate system is presented in Fig. 7 and a cut from this surface at  $z=4.1$  Å is shown in Fig. 8.

The derivative of the interaction energy along this coordinate can be interpreted as the frictional force along the naphthalene surface and is also plotted in Fig. 8 as a dotted line. The potential is symmetric around the origin while the force is antisymmetric. There are a number of optimum points where the force is zero. The very shallow local minimum found at  $\Delta x=0$  is due to the symmetric nature of the potential energy. The global minimum is at  $\Delta x=2.3$  Å and there is a local minimum at  $\Delta x=5.9$  Å with 0.49 kcal mol<sup>-1</sup> (with aug-cc-pVDZ basis). This local minimum corresponds to a structure supported by dispersion forces only. Once I<sub>2</sub> is projected on the  $x$ - $y$  plane, the nearest iodine atom is 2.1 Å away from the C-C bond. The barriers between global minimum and two local minima are 0.23 and 0.83 kcal mol<sup>-1</sup> respectively. At

**Table 3** Dimerization energy of naphthalene in the presence of I<sub>2</sub> (kcal mol<sup>-1</sup>)

N-N ( $z=3.6$ )	Dimer	I <sub>2</sub> (perpendicular)	I <sub>2</sub> (parallel)
	-7.31	-7.61	-7.39

**Table 4** Naphthalene dimer-I<sub>2</sub> interaction for both conformers (kcal mol<sup>-1</sup>)

	Perpendicular	Parallel
N-I <sub>2</sub>	-2.19	-0.72
N <sub>2</sub> -I <sub>2</sub>	-3.68	-1.62

room temperatures these barriers are very low to restrict I<sub>2</sub> molecule to the global minima, hence we should expect many different sites for I<sub>2</sub> to tag along. The motion along the *y*-axis is very harmonic as expected. A simple equation such as:

$$E(\Delta y) = -0.926829 + 0.33995 (\Delta y)^2 \quad (2)$$

describes the variation in the potential energy with 3-digit accuracy.

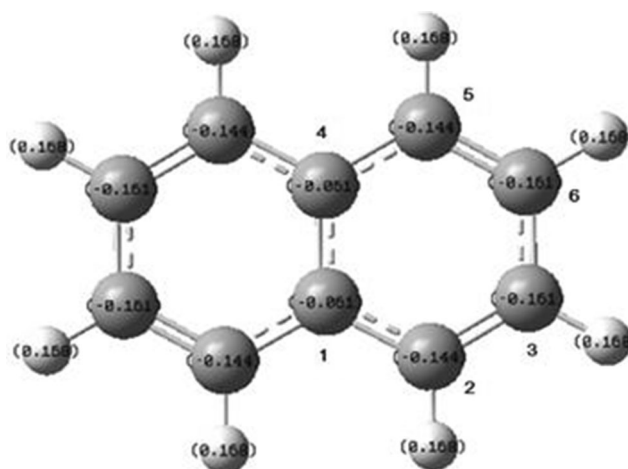
The third degree of freedom, namely the rotational angle, was investigated at two points in the ( $\Delta x$ - $\Delta y$ ) phase space, namely the global minimum and the local minimum where I<sub>2</sub> is at the center of naphthalene. In the first case, the rotation of I<sub>2</sub> around its center of mass was almost a free rotation; the full rotation required around 0.1 kcal mol<sup>-1</sup>. On the other hand, the rotation around the global minimum of the parallel conformation was relatively restricted. The rotational barrier was very close to 1.0 kcal mol<sup>-1</sup>. Of course, even this value does not prevent I<sub>2</sub> from accessing the naphthalene surface at different orientations.

#### Vibrational eigenvalues of 1-d potentials

For a better understanding of the stability of these weakly bound complexes, we calculated the vibrational eigenvalues of both approaches. First of all we looked for the harmonic frequency of both potentials. Keeping naphthalene and I<sub>2</sub> as single particles, we computed harmonic frequencies from  $V(z)$  around  $z_{eq}$ . The perpendicular approach has the fundamental frequency of  $1.0 \times 10^{12} \text{ s}^{-1}$ , which corresponds to a zero point energy of 0.049 kcal mol<sup>-1</sup>. The corresponding values for the shallow and floppy potential of the parallel conformation are  $7.1 \times 10^{11} \text{ s}^{-1}$  and 0.034 kcal mol<sup>-1</sup>. Since detailed curves for

**Table 5** Interaction energies of polyaromatic hydrocarbon (PAH)-I<sub>2</sub> complexes at SCS-MP2/aug-cc-pVDZ(C,H) and SCS-MP2/ECP-46MWB (I) (kcal mol<sup>-1</sup>). For Coronene, cc-pVDZ was used for C and H

	Perpendicular	Parallel
Naphthalene	2.19	0.72
Pyrene	4.44	3.27
Tetracene	2.70	1.98
Coronene	1.10	0.26

**Fig. 10** The natural bond order (NBO) charges of the naphthalene molecule

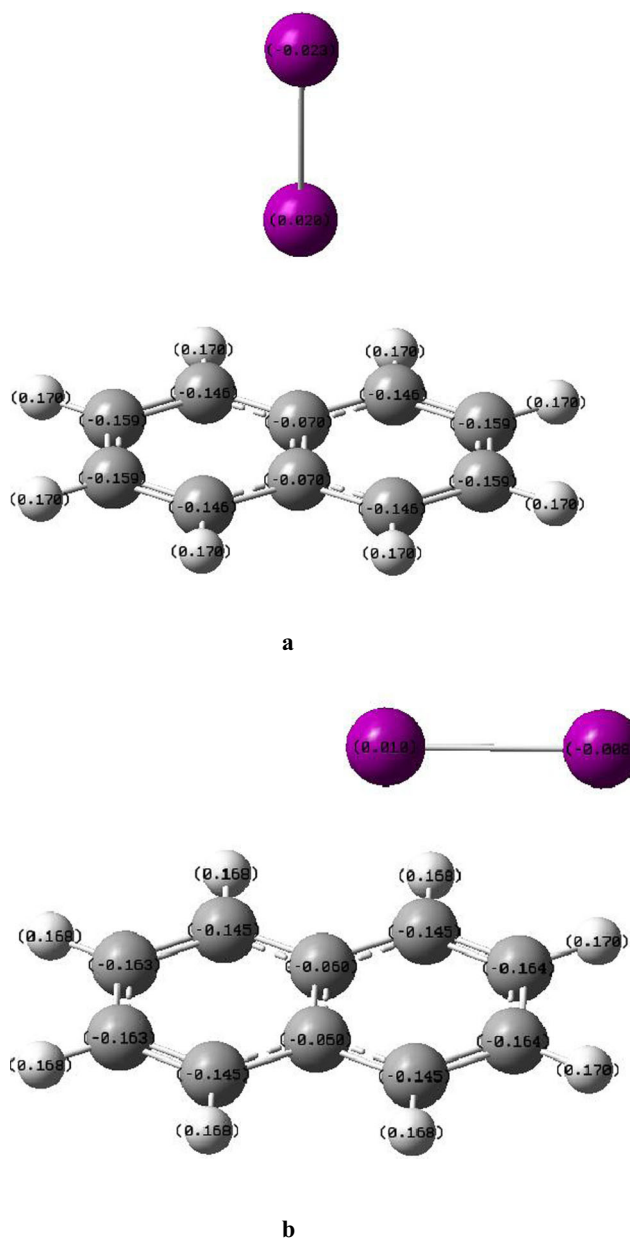
the potential energy were obtained, we proceeded to calculate all vibrational eigenvalues for nonrotating complexes. We used Le Roy's software LEVEL [30] to solve the vibrational eigenvalue problem. The perpendicular approach can hold 53 bound levels whereas the parallel conformation can support 25 eigenstates. The zero-point energy for the anharmonic potential was found to be 0.041 kcal mol<sup>-1</sup> and that of the parallel conformation is 0.034 kcal mol<sup>-1</sup>. A schematic diagram of the two potentials is given in Fig. 9.

#### Naphthalene dimer I<sub>2</sub> complexes

We carried out two calculations involving naphthalene dimer and I<sub>2</sub>. The first test was done to see whether surface adsorption of I<sub>2</sub> helps or hinders the exfoliation of PAH layers. Using SCS-MP2 with the aug-cc-pVDZ basis set, we calculated the interaction between two sandwiched naphthalene molecules. At  $z=3.6 \text{ \AA}$ , the interaction was found to be 7.31 kcal mol<sup>-1</sup>. Upon adsorbing I<sub>2</sub> on the surface of naphthalene, the dimerization of naphthalene remained unaffected (Table 3). For the second test, we calculated the strength of naphthalene-I<sub>2</sub> interactions again for both conformers and compared with a single naphthalene (Table 4). In this case the depth of the potential wells increase by 1.0–1.5 kcal mol<sup>-1</sup>, showing that the PAH-I<sub>2</sub> interaction is indeed very long range.

#### Edge effects

Naphthalene is a small molecule, thus the orientation of I<sub>2</sub> on the surface may be affected by being close to the edges. To test the effects of the presence of edges on the PAH-I<sub>2</sub> interaction, we carried out a small set of calculations with various PAHs. SCS-MP2 with the aug-cc-pVDZ basis set were used for these calculations.



**Fig. 11** NBO charges on the atoms of **a** perpendicular **b** parallel configurations

The results (presented in Table 5) vary in magnitude for different shaped molecules. For coronene, the augmented basis set was found to be linearly dependent, therefore we had to switch to the cc-pVDZ basis set. The relatively weak bonding may be due to the inadequacy of the basis set used.

We are in the progress of developing basis sets that will eliminate the linear dependency problem often met in noncovalent interactions as in  $\pi$ -stacking. Apart from this anomaly, the perpendicular conformation of  $I_2$  is found to be around  $1 \text{ kcal mol}^{-1}$  more stable than the parallel conformation. These results are not in accord with the findings of Rudenko et al. [31], in which the in-plane orientation of iodine with respect to a graphene-like supercell was found to be much more stable than the perpendicular orientation by taking into account the nonlocal correlation effects by means of vdW-DF-DFT methods.

The difference between a graphene-like sheet and PAH is of course significant; however, our results of larger PAHs show that the presence of hydrogens do not change the qualitative description of the interactions.

### NBO analysis

Natural bond order (NBO) analysis was performed to verify both the existence of charge transfer and its contribution to the total interaction energy. The MP2 method was used to perform this analysis for the naphthalene-iodine system in comparison to the neutral isolated naphthalene and iodine molecules (Fig. 10).

The iodine molecule also has two neutral iodine atoms as expected. NBO charges were calculated for both perpendicular and parallel geometries for comparison (Fig. 11).

The charge transfers were in the direction of donor (iodine)  $\rightarrow$  acceptor (naphthalene), i.e., from the lone pairs (LPs) of the iodine atom to the  $\pi$ -system of naphthalene as expected. This is a pure classical HOMO  $\rightarrow$  LUMO type charge transfer interaction, as summarized in Table 6.

The charge transfer was found higher for the perpendicular geometry, which is in accordance with the result that the perpendicular structure is more stable than the parallel one. The magnitude of the charge transfer energies were also reasonable in comparison to the total interaction energies. We would like to note that the charge transfer arguments presented here could also be interpreted as simple polarization effects since these two concepts are not mutually exclusive [32]. The perpendicular conformation of  $I_2$  is a typical example of halogen bonding where a positive potential on  $I_2$  is interacting with the negative potential of naphthalene ( $\sigma$  hole) as reported in the literature [33, 34].

**Table 6** Charge transfer (CT) energies ( $E$ ;  $\text{kcal mol}^{-1}$ ). LP Lone pair

	Donor	Acceptor	$E_{CT}$
Perpendicular	3 LPs of the nearest-neighbour iodine atom	$\pi^*$ (C1=C4)	0.19
Parallel	3 LPs of the nearest-neighbour iodine atom	$\pi^*$ (C2=C3) $\pi^*$ (C5=C6)	0.11



## Conclusions

We have carried out CCSD(T) calculations on various forms of naphthalene-I<sub>2</sub> supermolecules. The two possible approaches of iodine to the naphthalene surface were considered. The lower energy reaction path is the perpendicular approach keeping the C<sub>2v</sub> symmetry intact. The potential function for this approach can be expressed accurately as a simple Lennard-Jones interaction between naphthalene and iodine. The less stable conformation is obtained by placing I<sub>2</sub> parallel to the naphthalene surface. The local minimum for this interaction is at the symmetric orientation of iodine with respect to the long and short axes of naphthalene. A lower energy minimum of this surface is obtained by shifting I<sub>2</sub> along the long axis with 2.3 Å. The potential energy as a function of the I<sub>2</sub>-naphthalene center of masses can still be represented as a Lennard-Jones function.

In both approaches, potential wells are deep enough to support 53 and 25 vibrational levels. The potential around the minimum is found to be very harmonic upon comparing harmonic and anharmonic zero-point energies. ZPE are small enough not to challenge the stability of both conformers.

The interaction between naphthalene dimer and I<sub>2</sub> shows that naphthalene–naphthalene interaction is not affected by the presence of iodine. On the other hand, I<sub>2</sub> interacts strongly with the second layer of naphthalene. Finally we tested a few other PAH–I<sub>2</sub> complexes. Although our results are not exhaustive, we can safely state that perpendicular conformations of I<sub>2</sub> on a PAH surface are usually around 1 kcal mol<sup>-1</sup> more stable than in-plane conformations, with both approaches likely to be found with appropriate Boltzmann factors.

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## References

- Geim AK, Novoselov KS (2007) The rise of graphene. *Nat Mater* 6: 183
- Lee C, Wei XD, Kysar JW, Hone J (2008) Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 321: 385
- Fowler JD, Allen MJ, Tung VC, Yang Y, Kaner RB, Weiller BH (2009) Practical chemical sensors from chemically derived graphene. *ACS Nano* 3:2:01:306
- Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, Dai H (2000) Nanotube molecular wires as chemical sensors. *Science* 287: 622
- Lee SM, Lee YH (2000) Hydrogen storage in single-walled carbon nanotubes. *Appl Phys Lett* 76:2877
- Zhu XY, Lee SM, Lee YH, Frauenheim T (2000) Adsorption and desorption of an O<sub>2</sub> molecule on carbon nanotubes. *Phys Rev Lett* 85: 2757
- Jhi SH, Louie SG, Cohen ML (2000) Electronic properties of oxidized carbon nanotubes. *Phys Rev Lett* 85:1710
- Chang H, Do JL, Mi S, L, Hee Y (2001) Adsorption of NH<sub>3</sub> and NO<sub>2</sub> molecules on carbon nanotubes. *Appl Phys Lett* 79:3863
- Zhao J, Buldum A, Han J, Lu JP (2002) Gas molecule adsorption in carbon nanotubes and nanotube bundles. *Nanotechnology* 13:195
- Leenaerts O, Partoens B, Peeters FM (2008) Adsorption of H<sub>2</sub>O, NH<sub>3</sub>, CO, NO<sub>2</sub>, and NO on graphene: a first-principles study. *Phys Rev B* 77:125416
- Chen S, Cai W, Chen D, Ren Y, Li X, Zhu Y, Kang J, Ruoff RS (2010) Adsorption/desorption and electrically controlled flipping of ammonia molecules on graphene. *New J Phys* 12: 125011
- Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, Novoselov KS (2007) Detection of individual gas molecules adsorbed on graphene. *Nat Mater* 6:652
- Robinson JA, Snow ES, Badescu SC, Reinecke TL, Perkins FK (2006) Role of defects in single-walled carbon nanotube chemical sensors. *Nano Lett* 6: 8:1747
- Donchev AG (2007) Ab initio study of the effects of orientation and corrugation for H<sub>2</sub> adsorbed on polycyclic aromatic hydrocarbons. *J Chem Phys* 126:124706
- Medeiros PVC, Mascarenhas AJS, de Brito MF, de Castilho CMC (2010) A DFT study of halogen atoms adsorbed on graphene layers. *Nanotechnology* 21:485701
- Ghosh S, Yamijala SRKCS, Pati SK, Rao CNR (2012) The interaction of halogen molecules with SWNTs and graphene. *RSC Advances* 2:1181
- Werner HJ, Knowles PJ, Lindh R, Manby FR, Schu<sup>tz</sup> M, Celani P, Korona T, Rauhut G, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Lloyd AW, McNicholas SJ, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Schumann U, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T MOLPRO, version 2009.1, a package of ab initio programs, see <http://www.molpro.net>
- Bond length of I<sub>2</sub> molecule, in NIST chemistry web book. In: Howard WF, Andrews L (eds) NIST standard reference database number 69. National Institute of Standards and Technology, Gaithersburg, MD, 20899, (<http://webbook.nist.gov>)
- Yurtsever E (2009)  $\pi$ -stack dimers of small polyaromatic hydrocarbons: a path to the packing of graphenes. *J Phys Chem A* 113:924
- Yurtsever E (2010) Stacking of triphenylene: characterization of the potential energy surface. *Theo Chem Acc* 127:133
- Hobza P (ed) (2008) Non-standard base pairing and stacked structures in methyl xanthine clusters. *Phys Chem Chem Phys* 10:19: 2561:2868
- Grimme S (2003) Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies. *J Chem Phys* 118:9095
- Grimme S (2004) Accurate description of van der Waals complexes by density functional theory including empirical corrections. *J Comput Chem* 25:1463
- Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem* 27: 1787
- Jansen G, Haßelmann A (2001) Comment on: using Kohn-Sham orbitals in symmetry-adapted perturbation theory to investigate intermolecular interactions. *J Phys Chem A* 105:11156
- Haßelmann A, Jansen G (2002) First-order intermolecular interaction energies from Kohn-Sham orbitals. *Chem Phys Lett* 357:464
- Haßelmann A, Jansen G (2002) Intermolecular induction and exchange-induction energies from coupled-perturbed Kohn-Sham density functional theory. *Chem Phys Lett* 362:319
- Haßelmann A, Jansen G (2003) Intermolecular dispersion energies from time-dependent density functional theory. *Chem Phys Lett* 367: 778

29. Bergner A, Dolg M, Kuechle W, Stoll H, Preuss H (1993) Ab initio energy-adjusted pseudopotentials for elements of groups 13–17. *Mol Phys* 80:1431
30. LEVEL program, version 8.0, R.J. Le Roy 519: 888:4051. <http://leroy.uwaterloo.ca/programs/>
31. Rudenko AN, Keil FJ, Katsnelson MI, Lichtenstein AI (2010) Adsorption of diatomic halogen molecules on graphene: a van der Waals density functional study. *Phys Rev B* 82:035427
32. Politzer P, Riley KE, Bulat FA, Murray JS (2012) Perspectives on halogen bonding and other  $\sigma$ -hole interactions. *Comp Theo Chem* 998:2
33. Politzer P, Murray JS (2013) Halogen bonding: an interim discussion. *ChemPhysChem* 14:278
34. Politzer P, Murray JS, Clark T (2013) Halogen bonding and other  $\sigma$ -hole interactions: a perspective. *Phys Chem Chem Phys* 15:11178