Electronic Supporting Information
A density functional theory investigation of the adsorption of inorganic iodine species on graphitic surfaces

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S.1 Molecular Calculations

The adsorption energies calculated in sections 3.2-3.7 of the main text require the energy of the isolated molecule as an input quantity. This section of the supporting information describes the methods for obtaining these energies and gives the results of these calculations. The molecules investigated are I_2, HI, HOI, HIO_2, HIO_3, and CH_3I.

S.1.1 Computational Details

The Vienna *ab Initio* Simulation Package (VASP)[S1–S3] was used to perform spin-polarized Kohn-Sham density functional theory (DFT) calculations.[S4,S5] Molecular calculations were carried out in a 15Å by 15Å by 15Å box. The planewave kinetic energy cutoff was 900 eV, and only the gamma-point was sampled. The molecules were placed in the corner of the cell, and dipole corrections in the X-, Y-, and Z-directions were applied.

The projector augmented-wave[S6] method was used, and the standard potentials ('H', 'O', 'I', and 'C') from the VASP library[S7] were employed (see Table S.1 for the specific file names).

Table S.1: POTCAR file paths within the VASP PAW library

Element	POTCAR File
H	H/POTCAR
C	C/POTCAR
O	O/POTCAR
I	I/POTCAR

S.2 VASP Input Files

In addition to the POTCAR files mentioned in Section S.1.1, we provide example INCAR and KPOINTS files for the calculations. Many different types of systems were analyzed (bulk solid, slab, and molecule), so the INCAR file is annotated to indicate which flags are relevant in each situation. The same concept applies to choosing the method for computing the van der Waals interactions. The KPOINTS file is representative of the calculations, but the mesh must be changed based on the sizes specified in the main text and supporting informatoin.

S.2.1 INCAR File

```
SYSTEM=GRAPHITE

# Start/Restart parameters
ISTART = 0
ICHARG = 2
INIWAV = 1

# SCF Calculation Parameters
PREC   = Accurate
ENCUT  = 900
ALGO   = Normal
```

```
TIME   = 0.2
LSUBROT= .FALSE.
EDIFF  = 1E-06
NELM   = 200
NELMIN = 5
NELMDL = -4
ISPIN  = 2
LREAL  = .FALSE.
MAGMOM = 0 0 0 0
NBANDS = 24

# Brillouin Zone Integration and DOS Parameters
ISMEAR = 0
SIGMA  = 0.1
ISYM   = 0

# Ionic Relaxation Parameters
EDIFFG = -0.01
NSW    = 100
IBRION = 1
POTIM  = 0.5
ISIF   = 3     # set to 0 for molecules and slabs


# Parallelization Options
LPLANE = .TRUE.
LSCALU = .FALSE.
LSCALAPACK = .FALSE.
NCORE  = 4
KPAR   = 1

# Output Options
LCHARG = .FALSE.
LWAVE  = .FALSE.
LAECHG = .FALSE.
LORBIT = 11

# Dipole Corrections
#   Turn on (LDIPOL=.TRUE.) for slabs and molecules
#   For slabs, use IDIPOL=3 (assuming vacuum along c-axis)
#        Place slab near the bottom of the cell
#   For molecules, use IDIPOL=4 and place the molecule in the corner
#        of the cell (computationally more stable)
#LDIPOL = .TRUE.
#IDIPOL = 4

# Aspherical Corrections (needed for DFT-DF methods)
```

```
LASPH = .TRUE.

# Meta-GGA
# METAGGA = SCAN

# vDW corrections
# This input is set to use DFT-D3, but commenting/uncommenting
# the appropriate sections can activate DFT-DF, SCAN, or SCAN-RVV10
# calculations.
#
# DFT-D3
IVDW = 11

# DFT-DF (Langreth and Lundqvist et al.)
# Method reference: Dion et al. Phys. Rev. Lett. 92: 246401 (2004)
# Implementation Reference: Klimes et al. Phys. Rev. B 83: 195131 (2011)
# GGA = RE               # PE=PBE, RE=revPBE, OR=optPBE (for DFT-DF)
# LUSE_VDW = .TRUE.
# AGGAC = 0.0000
#
# SCAN + rVV10
# Method Reference: Phys. Rev. X 6: 041005 (2016)
#
# METAGGA=SCAN
# LUSE_VDW = .TRUE.
# BPARAM = 15.7
```

S.2.1.1 KPOINTS File

```
Graphite
0
Gamma
21 21 7
0.0 0.0 0.0
```

S.3 Structural and Vibrational Results

Both the SCAN functional and the SCAN+RVV10 calculations failed to produce vibrational frequencies.

Table S.2: Results for the I_2 molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond length (d_{I-I} in Å), and vibrational frequency (ν in cm^{-1}).

Functional/Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10	Experiment[S8]
d_{I-I}	2.6824	2.6824	2.7253	2.6674	2.6653	2.6655
ν	215	215	201	N/A	N/A	213

Table S.3: Results for the HI molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond length (d_{H-I} in Å), and vibrational frequency (in cm^{-1}).

Functional/Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10	Experiment [S8]
d_{H-I}	1.6255	1.6255	1.6295	1.6127	1.6126	1.6092
ν	2268	2268	2228	N/A	N/A	2230

Table S.4: Results for the HOI molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond lengths (d in Å), bond angles (θ in degrees), and vibrational frequencies (ν in cm^{-1}).

Functional/Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10	Experiment [S8]
d_{H-O_1}	0.9768	0.9768	0.9765	0.9681	0.9681	0.967
d_{O_1-I}	2.0054	2.0058	2.0328	1.9872	1.9867	1.994
θ_{H-O_1-I}	104.383	104.419	104.438	104.528	104.549	103.89
ν_1	3717	3717	3685	N/A	N/A	3626
ν_2	1061	1059	1067	N/A	N/A	1070
ν_3	569	568	536	N/A	N/A	575

Table S.5: Results for the HIO_2 molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond lengths (d in Å), bond angles (θ in degrees), dihedral angles (α in degrees), and vibrational frequencies (in cm^{-1}). No experimental data was found for the HIO_2 in the gas phase.

Functional/Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10
d_{H-O_1}	0.9785	0.9785	0.9785	0.9699	0.9698
d_{O_1-I}	2.0044	2.0044	2.0343	1.9813	1.9806
$d_{I=O_2}$	1.8279	1.8279	1.8444	1.8124	1.8121
θ_{H-O_1-I}	106.517	106.517	106.535	106.527	106.553
$\theta_{O_1-I=O_2}$	105.800	105.800	105.683	105.111	105.065
$\alpha_{H-O_1-I=O_2}$	82.0574	82.0574	80.5083	81.5726	81.5344
ν_1	3690	3690	3655	N/A	N/A
ν_2	996	995	1003	N/A	N/A
ν_3	781	781	744	N/A	N/A
ν_4	532	532	496	N/A	N/A
ν_5	360	359	352	N/A	N/A
ν_6	207	207	199	N/A	N/A

Table S.6: Results for the HIO_3 molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond lengths (d in Å), bond angles (θ in degrees), dihedral angles (α in degrees), and vibrational frequencies (in cm^{-1}). No experimental data was found for the HIO_3 in the gas phase.

Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10
d_{H-O_1}	0.9823	0.9823	0.9816	0.9743	0.9742
d_{O_1-I}	1.9754	1.9754	2.0051	1.9528	1.9522
$d_{I=O_2}$	1.7883	1.7883	1.8008	1.7718	1.7716
$d_{I=O_3}$	1.7848	1.7848	1.7982	1.7683	1.7679
θ_{H-O_1-I}	106.928	106.928	107.541	106.611	106.608
$\theta_{O_1-I=O_2}$	100.961	100.961	101.523	100.422	100.445
$\theta_{O_2=I=O_3}$	107.573	107.573	103.373	102.709	102.659
$\alpha_{H-O_1-I=O_2}$	28.7257	28.7257	33.3514	29.5039	29.1638
$\alpha_{H-O_1-I=O_3}$	82.4432	82.4432	77.9152	81.0337	81.2912
ν_1	3643	3643	3620	N/A	N/A
ν_2	937	936	948	N/A	N/A
ν_3	858	858	825	N/A	N/A
ν_4	831	831	798	N/A	N/A
ν_5	542	542	505	N/A	N/A
ν_6	292	293	285	N/A	N/A
ν_7	253	253	242	N/A	N/A
ν_8	220	220	213	N/A	N/A
ν_9	80	78	77	N/A	N/A

Table S.7: Results for the CH_3I molecule the PBE, PBE-D3, DFT-DF, SCAN, and SCAN-RVV10 methodologies. Bond lengths (d in Å), bond angles (θ in degrees), and vibrational frequencies (in cm^{-1}).

Method	PBE	PBE-D3	DFT-DF	SCAN	SCAN-RVV10	Experiment[S8]
d_{C-H}	1.0917	1.0918	1.0883	1.0834	1.0834	1.0840
d_{C-I}	2.1511	2.1531	2.1844	2.1379	2.1379	2.1358
θ_{H-C-I}	107.557	107.569	107.127	107.508	107.508	107.470
θ_{H-C-H}	111.343	111.323	111.695	111.376	111.377	111.396
ν_1	3140	3137	3129	N/A	N/A	3060
ν_2	3029	3025	3026	N/A	N/A	2933
ν_3	1420	1419	1452	N/A	N/A	1436
ν_4	1230	1230	1250	N/A	N/A	1252
ν_5	865	863	872	N/A	N/A	882
ν_6	528	524	495	N/A	N/A	533

S.4 Static Polarizability Study

To explore whether or not the strength of adsorption could be explained by London dispersion, we performed a supplemental examination of the static polarizability of the molecules in a vacuum using NWCHEM. For this supplemental study we opted to use the PBE functional, with the 6-311G** basis set. To ensure consistency the geometries were allowed to relax before performing the polarizability calculation. The results of the calculation are the electric dipole (μ), the isotropic static polarizability (α_{iso}), the anisotropic static polarizability (α_{aniso}) and the average static polarizability (α_{avg}). These are summarized in the table S.8 below:

Table S.8: Summary of results for the linear response calculation. Adsorption energy and graphite iodine distance are also displayed for reference. Adsorption energy is given in (kJ/mol), graphite iodine distance (d) in (Å), and all other data is in atomic units.

Molecule	HI	HIO_2	HIO_3	CH_3I	HOI	I_2
E_{ads}	21.2	23.4	23.9	28.9	30.8	33.1
d	3.52	3.79	3.93	3.69	3.68	3.73
α_{iso}	23.09	35.63	40.92	37.24	28.00	51.75
α_{aniso}	8.12	22.60	15.08	20.85	16.08	49.04
α_{avg}	23.09	35.63	40.92	37.24	28.00	51.75

The most promising trend we observe is that as as the isotropic polarizability increases so does the adsorption energy. However, CH_3I and HOI, don't follow the trend. CH_3I can plausibly be said to have a higher adsorption energy by being able to adsorb closer to the graphite. However, this would not be enough to explain why HOI has a higher adsorption energy than CH_3I, despite having nearly identical surface to iodine distance and a smaller polarizability. The most likely hypothesis in our opinion is that the relative location and orientation of the HOI above the graphite leads to a greater London dispersion force than would be predicted by a simple comparisons of the magnitude of the static isotropic polararizability. Further calculations exploring this are beyond the focus of this work, but may be explored in future studies.

In summary, while we do observe an apparent qualitative trend between isotropic polarizability and the adsorption energy, other factors such as orientations and distance prevent us from concluding a definitive qualitative trend.

References

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