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Biodetector for chlordane using doped InP₃ monolayers: a density functional theory study

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Chlordane is a serious pollutant in the environment, and it is necessary to monitor chlordane levels using biodetectors. We performed first-principles calculations to investigate the adsorption of chlordane on Ag, Pd, and Au doped InP₃ semiconductor monolayers. The results indicated that the adsorption energies of chlordane adsorbed on Ag, Pd, and Au doped InP₃ are −7.961 eV, −6.328 eV, and −7.889 eV respectively. The band gaps of the doped InP₃ monolayers underwent drastic changes after coming in contact with chlordane, the largest change in band gap occurred for Pd-doped InP₃, where the band gap changed from 0.024 eV to 0.335 eV. The large change in band gap shows that the monolayer is sensitive to the molecule, making it a good biodetector. Our results conclude that Pd-doped InP₃ stands out as the most promising biodetector for chlordane. This result will benefit environmental experimentalists in their further research.

1. Introduction

Pollution, with its far-reaching impacts on soil and water quality, poses a critical threat to public health and ecosystems worldwide. A common type of pollutant called persistent organic pollutants (POPs) has quickly become a global concern because of its detrimental effects on soil and water quality.¹ There are three main types of POPs, the first being industrial materials such as polychlorinated biphenyls (PCBs), industrial waste such as polyaromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs).² Organochlorine pesticides are synthetic pesticides that were widely used to control insect pests in agriculture and forestry all around the world.³ OCPs are banned in many parts of the world,³ classified as a type of neurotoxin,⁴ and an EDC (endocrine disrupting chemical)⁵ and can pose serious problems to one's health. Consequences of short-term exposure to these pesticides include convulsions, nausea, and tremors.⁶ Long-term exposure can cause an increased risk of dementia or Parkinson's disease;⁷ increased risk of certain cancers;⁸ and damage to the endocrine system.⁹ Although OCPs were banned decades ago, some remnants remain in the environment due to the persistent nature of the pesticides.¹⁰ A variety of such pesticides exist, some common examples include dichlorodiphenyltrichloroethane (DDT) for mosquito control,¹¹ endosulfan for fruit fly and larvae control,¹² and chlordane for termite control in homes.¹³ Chlordane was the second most important organochlorine insecticide, had an estimated annual production of nine million kilograms, and was used in millions of homes annually.¹⁴ It physically presents

as a thick, colourless or amber liquid, has a mild but irritating smell,¹⁵ and a chemical formula of C₁₀H₆Cl₈. It was banned in 1988 (ref. 16) but was used in lawns, homes, and agricultural fields as a form of pesticide and termite control.¹⁷ Chlordane is still a concern due to its ability to stick to soil,¹⁸ low solubility in water,¹⁷ and lipophilicity.¹⁹ It can still be found in treated areas, agricultural run-off water, and in the dust of buildings where it was once used.²⁰

Previous studies on chlordane covered a variety of topics, some examples being: its accumulation in people and animals as well as its persistence in nature. An earlier study on the accumulation of technical chlordane in fish and wildlife found that a concentration between 36.9–59 µg per 1 specimen is enough to cause a 50 percent mortality rate, concluding that chlordane is highly toxic.²¹ Oloff *et al.* conducted a study on OCP solubility and accumulation in nature and found that chlordane does not show any signs of metabolic breakdown over a 12 weeks period, demonstrating its danger to ecosystems.²² A study on the effects of chlordane on the human and rat liver concluded that chlordane caused an increase in levels of triglycerides (TG), creatine phosphokinase (CPK) and lactate dehydrogenase (LDH) as well as an increase in liver weight in both humans and rats.²³ Parada *et al.* investigated chlordane in relation to breast cancer survival and concluded that chlordane not only likely increases one's risk of cancer but also reduces one's survival rate.²⁴ Although there are many studies on the negative effects of chlordane on both living organisms and the environment, there are few studies on the detection and adsorption of chlordane to mitigate these risks.

A previous study by Qin *et al.*²⁵ explored the detection and adsorption of different OCPs from the environment using a pure InP₃ monolayer, but chlordane was not a part of this

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study. The lack of previous studies is evidence that the problem of chlordane pollution is often overlooked. However, it is important to be able to detect and absorb chlordane, a toxic chemical, from the environment for safety. One of the leading ways to do this is by using semiconductor monolayers, as shown from previous research.^{26,27} A semiconductor monolayer is a type of material that is a single molecule/atom in thickness made of a semiconductor.²⁸ Some common examples of semiconductor monolayers include: graphene,²⁹ MXene group,³⁰ and transition metal dichalcogenides (TMDs).³¹ An example of a group of semiconductor monolayers that may interact with chlordane is the aforementioned MXene group because they can conduct electricity³² and are highly biocompatible.³³ MXenes are a group of 2D transition metal carbide/nitride with a composition of $M_{n+1}X_nT_x$, where M is a transition metal, X is nitrogen or carbon, and T is a surface functional group.³⁴ However, more promising candidates for the detection and adsorption of chlordane are the allotropes SnP_3 ,³⁵ GeP_3 ,³⁶ and InP_3 (ref. 37) as shown from previous research. Specifically, the monolayer InP_3 is of great interest in being a sensitive detector for chlordane. Some of the previous applications of InP_3 are in lithium batteries,³⁸ the detection of various chemicals such as formaldehyde³⁹ and SF_6 ,⁴⁰ and the detection of certain organochlorine pesticides.²⁵

One of the many methods of detection and adsorption for organochlorine pesticides is using doped semiconductor monolayers.⁴¹ For chlordane specifically, InP_3 (indium triphosphide) is a promising candidate because of its graphene-like structure, high electron mobility, chemical stability and adjustable band gap.⁴² Furthermore, the In–P bond also shows strong attraction to select polar molecules because of its polar covalent nature, making it a sensitive detector.²⁵ A graphene-like structure is especially beneficial for sensing because of its excellent adsorption property,⁴³ high conductivity of both heat and electricity⁴⁴ and large specific surface area.⁴⁵ A large specific surface area means that there is a high density of receptors in a given area, making the material sensitive. To optimize InP_3 for chlordane detection, its band gaps are adjusted using palladium (Pd), gold (Au) and Silver (Ag) based on previous research. Palladium was chosen based on previous research showing improved sensitivity to CO, NH_3 , O_2 and NO_2 when doped into graphene.^{46,47} This is important as the chemical formula of chlordane is $C_{10}H_6Cl_8$, so it is vital that the modified InP_3 monolayer is sensitive to its elements C, H and Cl. Next, gold was selected based on previous research demonstrating its affinity for modifying monolayers to be more sensitive to chlorine.⁴⁸ Silver was selected due to its previously shown ability to modify InP_3 to be more sensitive to NO_2 .⁴⁷ This study hopes that by modifying InP_3 , the detection and adsorption of chlordane can be more effective.

The density functional theory (DFT) is used in this study to analyze the effectiveness of each dopant (Ag, Pd, Au) in modifying the InP_3 monolayer for detecting chlordane ($C_{10}H_6Cl_8$). Calculations were conducted to find the optimal electronic and atomic structure of each complex. The results were then analyzed and the different monolayers were compared to find the most optimal for detecting chlordane.

II. Method

A. Computational details

The density functional theory (DFT) incorporated into the ABINIT package⁴⁹ implements the generalized gradient approximation (GGA)⁵⁰ exchange–correlation functionals with a Perdew–Burke–Ernzerhof (PBE) format. The projected augmented wave (PAW) method⁵¹ is used to produce pseudo-potentials using the AtomPAW⁵² code. The electron configurations of hydrogen (H), carbon (C), phosphorus (P), chlorine (Cl), palladium (Pd), silver (Ag), indium (In), and gold (Au) are shown in Table 1.

B. Convergence details

In the total energy calculation, the self-consistent field (SCF) cycle stopped once the total energy difference was less than 1.0×10^{-10} Ha twice consecutively. The convergence of kinetic energy cutoff, Monkhorst–Pack⁵³ k -point grids, and vacuum layer was also calculated. The convergence criterion was fulfilled when the total energy difference of datasets was smaller than 0.0001 Ha (0.003 eV) twice consecutively.

Using the Broyden–Fletcher–Goldfarb–Shanno minimization (BFGS)⁵⁴ structural optimization of the chlordane molecule, pure indium triphosphide monolayer, Au-, Pd-, Ag-doped monolayers, and their complex systems were performed. The tolerance for the maximum force of each atom is less than 2.0×10^{-3} Ha/Bohr (0.01 eV \AA^{-1}). The SCF cycle will be terminated once the force difference is smaller than 1.0×10^{-10} Ha/Bohr (0.01 eV \AA^{-1}) twice consecutively.

C. Atomic structure

The structure of *cis*-chlordane, with a chemical formula of $C_{10}H_6Cl_8$ was optimized along with the primitive cell of InP_3 . The process was repeated with the $3 \times 3 \times 1$ monolayer InP_3 with 32 total atoms (8In, 24P) and interstitial doping of the monolayer by placing the dopant (an atom of Ag, Pd, and Au) in the center of the monolayer – its most optimal spot – created the doped $3 \times 3 \times 1$ supercell. The substrates are then optimized according to the aforementioned convergence requirements. The defect formation energy (given by E_f) of an atom on InP_3 is given by

$$E_f = E_{\text{Dopant/monolayer}} - E_{\text{monolayer}} - E_{\text{Dopant}} \quad (1)$$

Table 1 Electron configurations and radius cutoffs of elements used in current research

Element	Configuration	Radius cutoff (Bohrs)
Hydrogen (H)	1s ¹	1.00
Carbon (C)	[He]2s ² 2p ²	1.32
Phosphorus (P)	[Ne]3s ² 3p ³	1.85
Chlorine (Cl)	[Ne]3s ² 3p ⁵	1.49
Palladium (Pd)	[Kr]4d ¹⁰	3.19
Silver (Ag)	[Kr]4d ¹⁰ 5s ¹	3.12
Indium (In)	[Kr]4d ¹⁰ 5s ² 5p ¹	2.95
Gold (Au)	[Xe]6s ¹ 4f ¹⁴ 5d ¹⁰	3.29



where $E_{\text{Dopant/monolayer}}$ is the total energy of the monolayer, $E_{\text{monolayer}}$ is the total energy of the $3 \times 3 \times 1$ InP₃ monolayer, and E_{Dopant} is the total energy of the pure element.⁵⁵ Next, chlordanes were placed on top of the optimized monolayers in a manner that maximized the amount of chlorine interaction with the monolayer/dopant.

D. Electronic structure

1. Band structure. The band structures were computed along the high symmetry k -points Γ (0, 0, 0), M (1/2, 0, 0), K (1/3, 2/3, 0), and Γ (0, 0, 0). The converged charge density values of optimized structures of the monolayer (pure and doped with Ag, Pd, Au) were used to calculate the band structure. Next, a similar process is repeated for the complex system of chlordanes placed on the different monolayers.

2. Projected density of state. To analyze chlordanes adsorption on pure, Ag-doped, Pd-doped, and Au-doped monolayers, calculations of the projected density of states (PDOS) were conducted using the tetrahedron method. The atoms for the calculations were selected based on their proximity to the gas exchange site.

3. Charge transfer. Furthermore, the interactions between chlordanes and the different substrates are further analyzed by calculating the charge transfer between the atoms. The equation for charge transfer is represented as

$$\Delta\rho = \rho_{\text{molecule/monolayer}} - \rho_{\text{monolayer}} - \rho_{\text{molecule}} \quad (2)$$

where $\Delta\rho$ represents the net charge transfer and $\rho_{\text{molecule/monolayer}}$, $\rho_{\text{monolayer}}$, ρ_{molecule} represent the charge density of the chlordanes-substrate system, the substrate, and the molecule respectively.⁵⁶

4. Biodetector sensability. Sensing response is vital for a biodetector and can be calculated with the equation

$$S = \frac{\sigma_{\text{monolayer+molecule}}^{-1} - \sigma_{\text{monolayer}}^{-1}}{\sigma_{\text{monolayer}}^{-1}} \quad (3)$$

where S is the sensing response, $\sigma_{\text{monolayer+molecule}}$ and $\sigma_{\text{monolayer}}$ indicate the conductivity of the chlordanes + monolayer and the monolayer system respectively.⁵⁷ The electrical conductivity (σ) of the InP₃ systems can be calculated with the equation:

$$\sigma \propto \exp(-E_g/2k_B T) \quad (4)$$

where E_g , k_B , and T represent the band gap of the different substrates, the Boltzmann constant, and the temperature (room temperature is 300 K) respectively.⁵⁸

E. Adsorption calculations

The optimized chlordanes structure was placed on top of the various prepared monolayers and the adsorption energies were calculated:

$$E_{\text{ad}} = E_{\text{molecule+monolayer}} - E_{\text{monolayer}} - E_{\text{molecule}} \quad (5)$$

in which E_{ad} , $E_{\text{mol+monolayer}}$, $E_{\text{monolayer}}$, and E_{mol} represent the adsorption energy, the total energy of chlordanes added to the

total energy of the InP₃ monolayer system, InP₃ monolayer, and the chlordanes molecule, respectively.⁵⁵

III. Results

The structural and adsorption properties before and after the adsorption of chlordanes molecule onto the pure InP₃ monolayer were analyzed first to use as a point of reference. Next, Ag, Pd, and Au are interstitially doped onto the pure monolayer to improve the adsorption of chlordanes into InP₃. Then, the adsorption energy, band structure, sensibility, PDOS, and charge transfer of the doped monolayers were calculated to assess their affinity for detecting and absorbing chlordanes. The optimized structures of chlordanes (C₁₀H₆Cl₈) and InP₃ primitive cell are shown in Fig. 1. The calculated structural parameters are shown in Table 2 and are in good accordance with other theoretical studies.^{55,59} To find the most optimal structure of InP₃ substrate, 2×2 , 3×3 , and 4×4 supercells were tested and it was found that the 3×3 supercell was optimal according to the aforementioned convergence requirements. Using the optimized atomic configurations, the band structures of the 3×3 pristine and doped InP₃ are calculated and presented in Fig. 2 and Table 3. Pristine InP₃ has an indirect band gap of 0.703 eV,

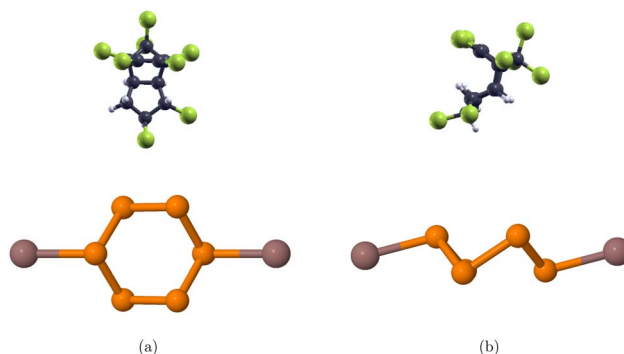


Fig. 1 Optimized structures of chlordanes (a) top view of chlordanes molecule and InP₃ primitive cell (b) side view of chlordanes molecule and InP₃ primitive cell. Navy, white, green, orange, and brown colors are used to represent carbon, hydrogen, chlorine, phosphorus, and indium respectively.

Table 2 Calculated and experimental results for the structural parameters of the chlordanes molecule and the InP₃ monolayer

	Bond lengths and bond angles	Current study (Å)	Other study (Å)
C ₁₀ H ₆ Cl ₈	C–Cl	1.76	1.84 (ref. 59)
	C–H	1.10	
	C–C (double bond)	1.57	
	C–C (single bond)	1.54	
	∠ C–C–C	108.2°	117 (ref. 59)
InP ₃	∠ Cl–C–Cl	107.9°	107.2 (ref. 59)
	P–P	2.24	2.24 (ref. 55)
	In–P	2.57	2.53 (ref. 55)
	∠ P–in–P	113.3°	113.3° (ref. 55)
	∠ P–P–P	92.8°	92.2° (ref. 55)



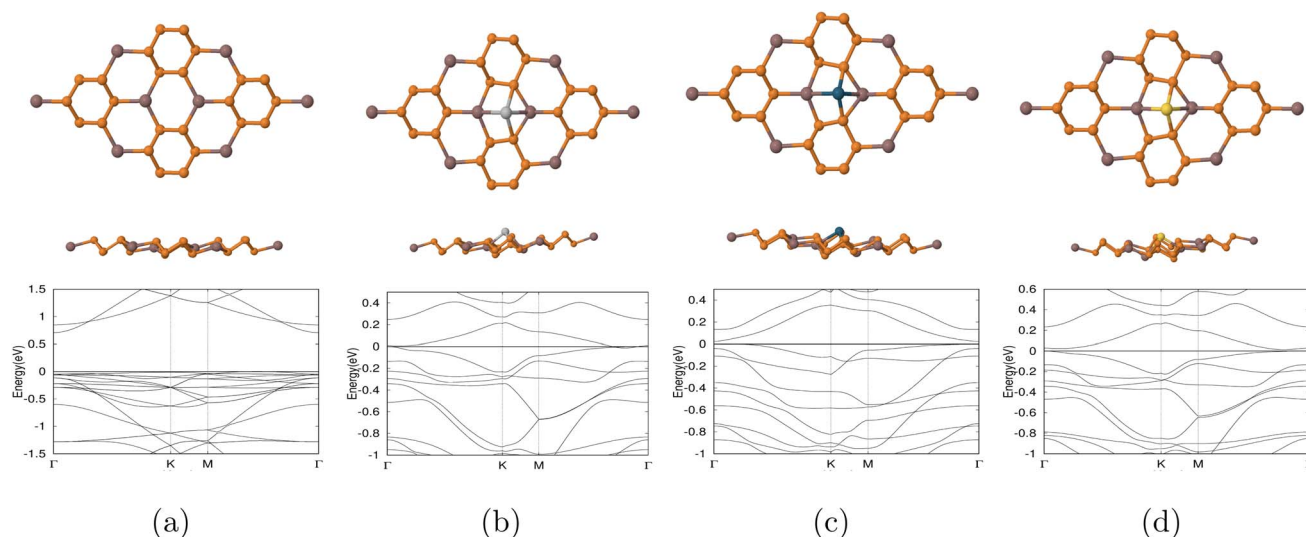


Fig. 2 Optimized structures of top and side view of (a) pure $3 \times 3 \times 1$ InP_3 monolayer (b) Ag-doped $3 \times 3 \times 1$ InP_3 monolayer (c) Pd-doped $3 \times 3 \times 1$ InP_3 monolayer (d) Au-doped $3 \times 3 \times 1$ InP_3 monolayer. Orange, brown, silver, blue, and gold, represent phosphorus, indium, silver, palladium, and gold respectively.

Table 3 Optimized structural parameters for pure and doped $3 \times 3 \times 1$ InP_3 monolayers: bond lengths (d), lattice constant (a), band gap (E_g), band gap after chlordan contact (c), and deformation energy (E_f)

Substrate	d (Å)	a (Å)	E_g (eV)	E_f (eV)
InP_3	—	28.5019	0.703	0.25267
Ag-doped InP_3	Ag-P 2.64 Ag-In 2.99	28.461	0	0.253
Pd-doped InP_3	Pd-P 2.35 Pd-In 2.85	28.362	0.024	0.342
Au-doped InP_3	Au-P 2.5 Au-In 2.95	28.463	0.013	0.336

Ag doped InP_3 has a band gap of 0, Pd doped InP_3 has a direct band gap of 0.024 eV, and Au doped InP_3 has an indirect band gap of 0.013 eV.

Chlordan was oriented and placed centrally on top of the substrate in a manner that guarantees as many as possible interactions between its Cl atoms and the substrate's dopant and indium atoms. It is known that InP_3 interacts well with polar molecules such as chlordan. By orienting chlordan so that the maximum amount of chlorine atoms (3) is facing toward the substrate, chlorine can more easily interact with the metal dopants and indium. Note that a chemical reaction does

Table 4 The adsorption energy (E_{ad}), bond length between chlordan and dopant (d), band gap (E_g) between chlordan and the substrates

System	E_{ad} (eV)	d (Å)	E_g (eV)
InP_3	−0.065	—	0.683
Ag-doped InP_3	−7.961	2.970	0
Pd-doped InP_3	−6.328	2.350	0.335
Au-doped InP_3	−7.889	3.18	0

not occur as the dissociation energy for chlordan bonds is larger than the calculated adsorption energies (E_{ad}). After relaxation, the adsorption energy (E_{ad}), bond length between Cl and the dopant, and band gap (E_g) for each complex system are calculated and shown in Table 4. The relaxed structures are shown in Fig. 3. A positive adsorption energy indicates an endothermic reaction with a non-spontaneous adsorption while

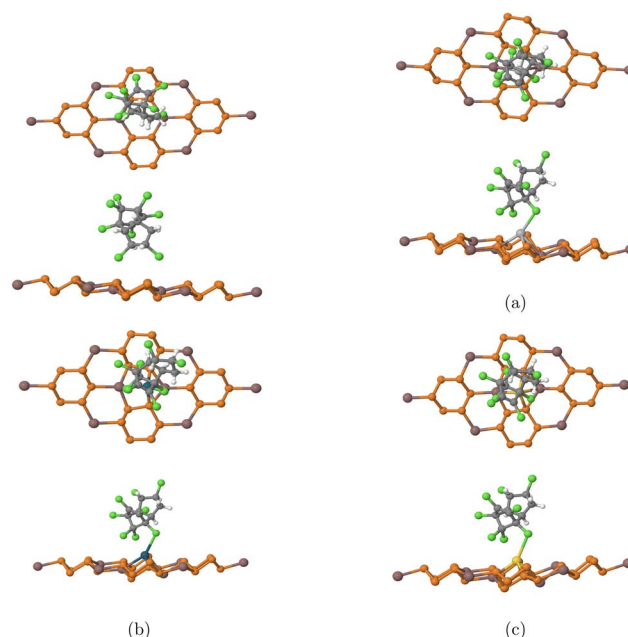


Fig. 3 Optimized structures of top and side view of the systems investigated in this study: chlordan placed on top of (a) pure InP_3 monolayer (b) Ag-doped InP_3 monolayer (c) Pd-doped InP_3 monolayer (d) Au-doped InP_3 monolayer. Gray, white, green, orange, brown, light gray, blue, and gold, represent carbon, hydrogen, chlorine, phosphorus, indium, silver, palladium, and gold respectively.



a negative adsorption energy indicates an exothermic reaction with a spontaneous adsorption.⁴⁷ The more negative the adsorption energy is, the stronger the interaction between chlordanes and InP₃ substrates would be.⁴⁷ The comparatively less negative adsorption energy value (eV) for the interaction between chlordanes and pristine InP₃ indicates a weaker interaction between the two, signifying that pristine InP₃ would not make a great detector for chlordanes. Comparatively, a smaller adsorption energy value between Ag-doped InP₃, Au-doped InP₃ and chlordanes suggests that both have strong interactions with chlordanes while Pd-doped InP₃ has a slightly weaker interaction with chlordanes given its less negative adsorption value. To determine if a material is sensitive to a molecule, the change in band gap (before/after coming in contact with the molecule) must be considered. The most significant change in band gap is seen in Pd-doped InP₃ where the gap changed from 0.024 eV to 0.335 eV, likely suggesting that Pd-doped InP₃ is sensitive to chlordanes. Next, the band gap of Au-doped InP₃ changed from 0.013 eV to 0, signifying that after coming in contact with chlordanes, the material may have become metallic. A metallic material is also extremely good for sensing of its high conductivity, which when used in eqn (3) means that the material is sensitive to the compound. However, the band gap for Ag-doped

InP₃ remains unchanged from 0 to 0, and it is impossible to know for certain if the material is sensitive to chlordanes. Pristine InP₃ underwent very little change after coming in contact with chlordanes and the structure remains unchanged, suggesting limited chlordanes sensitivity. The change in band gaps before and after contact with chlordanes is shown in Table 5.

The projected density of states (PDOS) for each complex was graphed and shown in Fig. 4. For the pristine InP₃ notable hybridization of the orbitals occurs below Fermi level at 0.005 eV, and 1.28 eV, marking 2 hybridization points. Comparatively, notable hybridization occurs at many more points for all of the other substrates. Specifically, for Ag-doped InP₃ significant hybridization occurs below Fermi level at 0.2 eV, 0.9 eV, and 1.01 eV; Au-doped InP₃ shows hybridization at 0.21 eV and below Fermi level at 0.1 eV and 0.7 eV; and Pd-doped InP₃ shows hybridization at −0.01 eV, −0.3 eV, and −0.7 eV. The numerous hybridization sites of the different orbitals across all the graphs indicate a strong interaction between chlordanes and the various doped substrates. Obviously, pristine InP₃ has less hybridization with the chlordanes molecule as shown in Fig. 5a aligns with the previous evidence that pristine InP₃ is not the optimal detector for chlordanes. The calculated PDOS results are in strong agreement with the band structures and adsorption energy calculations.

Using eqn (2), the charge transfer isosurfaces between the chlordanes molecule and substrates are shown in Fig. 5. Electrons deplete around the dopant and accumulate around the chlorine atoms. Comparatively, there is a slightly greater electron exchange between the Pd-doped InP₃ and chlordanes than the other doped substrates. Notably, the pristine InP₃ has very little electron transfer between the chlordanes molecule, aligning with previous conclusions that pristine InP₃ is not a good detector for chlordanes. Although all three doped InP₃ substrates demonstrate strong chemisorption, pristine InP₃ shows

Table 5 The band gaps of the pure and doped InP₃ monolayers before and after interacting with chlordanes

System	Band gap before chlordanes (E_g) (eV)	Band gap after chlordanes (E_g) (eV)
InP ₃	0.703	0.683
Ag-doped InP ₃	0	0
Pd-doped InP ₃	0.024	0.335
Au-doped InP ₃	0.013	0

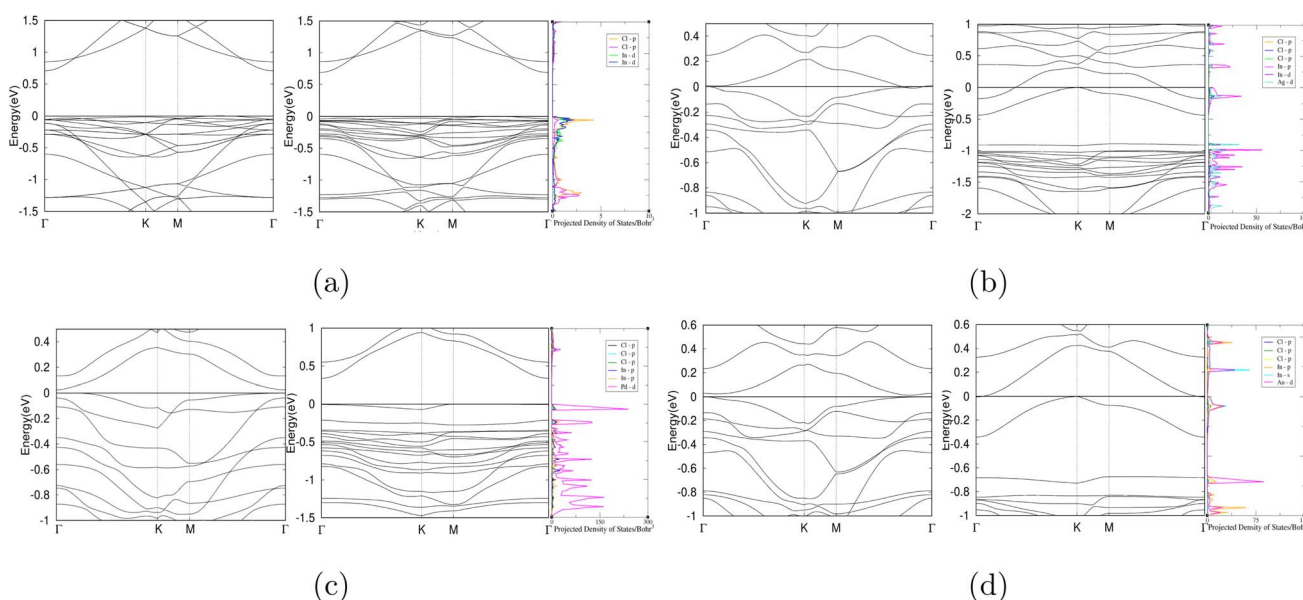


Fig. 4 Band structures and PDOS graphs of chlordanes on (a) pure InP₃ monolayer (b) Ag-doped InP₃ monolayer (c) Pd-doped InP₃ monolayer (d) Au-doped InP₃ monolayer. Refer to the legend on each individual PDOS graph for the representation of the different atoms and orbitals.

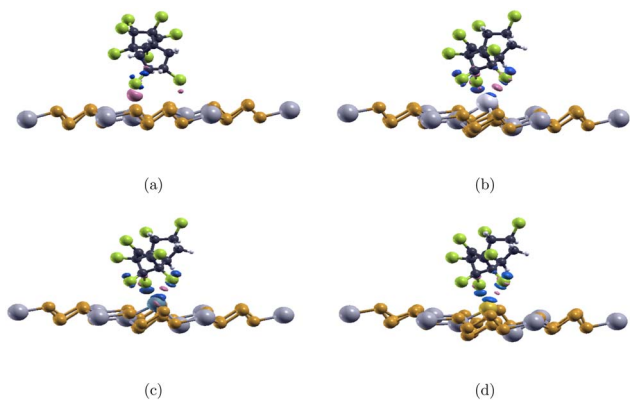


Fig. 5 Charge transfer of chlordanes on (a) pure InP_3 (b) Ag-doped InP_3 (c) Pd-doped InP_3 (d) Au-doped InP_3 . The pink areas indicate electron accumulation, while the blue regions show electron depletion. The gray, orange, green, navy blue, white, light gray, turquoise, and yellow colors represent In, P, Cl, C, H, Ag, Pd, Au, respectively. The isovalue is set at 0.015 electron/Bohr³.

physisorption which further supports conclusions that pristine InP_3 is not a great detector for chlordanes.

IV. Conclusion

In summary, pristine and doped InP_3 were investigated using density functional theory to explore the most optimal detector for chlordanes. We calculated the adsorption energy, band structure, projected density of states, and charge difference before and after chlordanes adsorption.

While all 3 doped monolayers are capable of adsorbing chlordanes, Ag doped InP_3 has the best adsorption value at -7.961 eV and pure InP_3 has the worst adsorption value at -0.065 eV. The greatest band gap change occurred for Pd doped InP_3 where it changed from 0.024 eV to 0.335 eV after interacting with chlordanes. Given Pd doped InP_3 's good adsorption value at -6.328 eV and its large change in band gap, it is the most promising substrate.

Data availability

Data for this article, including the PAW datasets used are available on the ABINIT website at <https://www.abinit.org/>. The code for ABINIT can be found at https://abinit.github.io/abinit_web/download.html with DOI-<https://doi.org/10.1016/j.cpc.2019.107042>. The version of the code employed for this study is version 10.0.7. The ATOMPAW code used to generate the pseudopotentials can be found at <https://github.com/atompaw> with DOI-[https://doi.org/10.1016/S0010-4655\(00\)00244-7](https://doi.org/10.1016/S0010-4655(00)00244-7). The XCrySDen program used to process figures can be found at <http://www.xcrysden.org/Download.html> with DOI-[https://doi.org/10.1016/S1093-3263\(99\)00028-5](https://doi.org/10.1016/S1093-3263(99)00028-5).

Conflicts of interest

There are no conflicts to declare.

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