



AFRL-RX-WP-JA-2014-0158

**DENSITY FUNCTIONAL THEORY STUDY OF
CHEMICAL SENSING ON SURFACES OF SINGLE-
LAYER MOS₂ AND GRAPHENE (POSTPRINT)**

**Ruth Pachter
AFRL/RXA**

**APRIL 2014
Interim Report**

Distribution A. Approved for public release; distribution unlimited.

See additional restrictions described on inside pages

STINFO COPY

© 2014 AIP Publishing LLC

**AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE**

NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the USAF 88th Air Base Wing (88 ABW) Public Affairs Office (PAO) and is available to the general public, including foreign nationals.

Copies may be obtained from the Defense Technical Information Center (DTIC)
(<http://www.dtic.mil>).

AFRL-RX-WP-JA-2014-0158 HAS BEEN REVIEWED AND IS APPROVED FOR
PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

//Signature//

RUTH PACTER
Senior Scientist
Functional Materials Division

//Signature//

TIMOTHY J. BUNNING, Chief
Functional Materials Division
Materials and Manufacturing Directorate

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Defense, Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) April 2014		2. REPORT TYPE Interim		3. DATES COVERED (From - To) 28 March 2013 – 29 March 2014	
4. TITLE AND SUBTITLE DENSITY FUNCTIONAL THEORY STUDY OF CHEMICAL SENSING ON SURFACES OF SINGLE-LAYER MOS ₂ AND GRAPHENE (POSTPRINT)				5a. CONTRACT NUMBER FA8650-09-D-5430-0025	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 62102F	
6. AUTHOR(S) (see back)				5d. PROJECT NUMBER 4347	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER X0KU	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) (see back)				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Materials and Manufacturing Directorate Wright Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/RXA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RX-WP-JA-2014-0158	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A. Approved for public release; distribution unlimited. This report contains color.					
13. SUPPLEMENTARY NOTES PA Case Number: 88ABW-2014-0840; Clearance Date: 3 March 2014. Journal article published in The Journal of Applied Physics 115, 164302 (2014). © 2014 AIP Publishing LLC. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display or disclose the work. The final publication is available at http://dx.doi.org/10.1063/1.4871687 .					
14. ABSTRACT In this work, density functional theory (DFT) calculations have been used to investigate chemical sensing on surfaces of single-layer MoS ₂ and graphene, considering the adsorption of the chemical compounds triethylamine, acetone, tetrahydrofuran, methanol, 2,4,6-trinitrotoluene, o-nitrotoluene, o-dichlorobenzene, and 1,5-dichloropentane. Physisorption of the adsorbates on free-standing surfaces was analyzed in detail for optimized material structures, considering various possible adsorption sites. Similar adsorption characteristics for the two surface types were demonstrated, where inclusion of a correction to the DFT functional for London dispersion was shown to be important to capture interactions at the interface of molecular adsorbate and surface. Charge transfer analyses for adsorbed free-standing surfaces generally demonstrated very small effects. However, charge transfer upon inclusion of the underlying SiO ₂ substrate rationalized experimental observations for some of the adsorbates considered. A larger intrinsic response for the electron-donor triethylamine adsorbed on MoS ₂ as compared to graphene was demonstrated, which may assist in devising chemical sensors for improved sensitivity.					
15. SUBJECT TERMS chemistry, computational, computer analysis, laser hardening, material development, nanotechnology, physics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor) Ruth Pachter
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (937) 255-9689
			SAR	12	

REPORT DOCUMENTATION PAGE Cont'd

6. AUTHOR(S)

R. Pachter - Materials and Manufacturing Directorate, Air Force Research Laboratory, Functional Materials Division
F. Mehmood - General Dynamics Information Technology, Inc.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

AFRL/RXA
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750

General Dynamics Information Technology, Inc.
Dayton, Ohio 45431

Density functional theory study of chemical sensing on surfaces of single-layer MoS₂ and graphene

F. Mehmood and R. Pachter^{a)}

Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, USA

(Received 27 February 2014; accepted 29 March 2014; published online 22 April 2014)

In this work, density functional theory (DFT) calculations have been used to investigate chemical sensing on surfaces of single-layer MoS₂ and graphene, considering the adsorption of the chemical compounds triethylamine, acetone, tetrahydrofuran, methanol, 2,4,6-trinitrotoluene, o-nitrotoluene, o-dichlorobenzene, and 1,5-dichloropentane. Physisorption of the adsorbates on free-standing surfaces was analyzed in detail for optimized material structures, considering various possible adsorption sites. Similar adsorption characteristics for the two surface types were demonstrated, where inclusion of a correction to the DFT functional for London dispersion was shown to be important to capture interactions at the interface of molecular adsorbate and surface. Charge transfer analyses for adsorbed free-standing surfaces generally demonstrated very small effects. However, charge transfer upon inclusion of the underlying SiO₂ substrate rationalized experimental observations for some of the adsorbates considered. A larger intrinsic response for the electron-donor triethylamine adsorbed on MoS₂ as compared to graphene was demonstrated, which may assist in devising chemical sensors for improved sensitivity. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871687>]

I. INTRODUCTION

Two-dimensional atomic crystals have recently emerged as an alternative to graphene, showing improved attributes in some cases.¹ Transition metal dichalcogenides have, in particular, drawn attention for application.² Recently, semiconducting single-layer MoS₂ (SL-MoS₂) field effect transistors (FETs) demonstrated some improvement in ON/OFF current ratio and relatively high mobilities,^{3–6} however, transport could be complicated by localized states⁷ or atmospheric adsorbates.⁸ On the other hand, for practical applications, MoS₂ FETs emerged as promising for chemical sensing, e.g., of NO,^{9,10} or NO₂ and NH₃.¹¹ Changes in conductance upon chemical adsorption on SL MoS₂ flakes in comparison to graphene for various analytes demonstrated a robust response.¹² A relatively large change in sensitivity was noted for the electron-donor triethylamine (TEA) by Perkins *et al.*,¹² while the response to electron-acceptors was minimal. SL-MoS₂ FETs are known to exhibit *n*-type doping although the origin of it remains mostly unclear, presumably due to impurities.¹³ Unlike SL-MoS₂, SL-graphene is known to exhibit *p*-doping.^{14,15} Indeed, as we previously pointed out,¹⁶ understanding the behavior of a nano-FET is complicated by various scatterers, thus necessitating understanding of the intrinsic mechanism of an analyte's adsorption, which can be achieved, in part, by computational prediction. Because MoS₂ could become a two-dimensional material of choice for chemical sensing, we aim in this work to systematically examine parameters that may affect the electronic structure upon molecular adsorption, both on MoS₂ and for comparison on graphene surfaces. Theoretical work has been limited so far, with a few examples for either adsorbates^{14,17} or interaction with the substrate^{15,18–20} for one type

of surface, while MoS₂ vs. graphene has not been consistently assessed for chemical sensing application.

In this work, we applied density functional theory (DFT) for a comprehensive and consistent investigation of organic compound physisorption on model surface systems of graphene and MoS₂. Effects of inclusion of a SiO₂ substrate to model a realistic material were also examined for selected cases. Various adsorbates, including those used in the experimental work of Perkins *et al.*,¹² i.e., electron-donor and acceptor molecules, as well as solvents of varying polarity, were considered. Physisorption characteristics were analyzed in detail, where optimized hybrid material system structures were elucidated for the molecular adsorbates triethylamine, acetone (ACE), tetrahydrofuran, methanol, 2,4,6-trinitrotoluene (TNT), o-nitrotoluene, o-dichlorobenzene, and 1,5-dichloropentane. Charge transfer analyses in the optimized surface—chemical adsorbate systems provided partial rationalization of observed sensing trends for some molecules upon inclusion of a substrate, and have shown that a MoS₂-based FET could potentially consist of a more sensitive platform for electron-donating chemical groups. Indeed, local density of states (LDOS) results demonstrated small effects upon adsorption, however, showing a relatively stronger response for an electron-donor upon inclusion of the underlying SiO₂ substrate.

II. COMPUTATIONAL DETAILS

DFT calculations^{18,19} were carried out by solving the Kohn-Sham equations¹⁹ using the Vienna ab initio simulation package (VASP).^{20,21} The electron-ion interactions for Mo, S, C, O, N, Cl, and H were described by projector augmented plane wave (PAW) potentials.²² A plane-wave energy cutoff of 400 eV was used for all calculations, found to be sufficient for these systems.²³ The generalized gradient

^{a)}Author to whom correspondence should be addressed. Electronic address: ruth.pachter@us.af.mil

approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used,²⁴ and the vdW-DF²⁵ non-empirical correction was applied to correct for London dispersion upon molecular adsorption. Considering the large size of some of the molecules, a large 8×8 supercell was modeled with planar dimensions of $19.7 \times 17.1 \text{ \AA}^2$ for SL-graphene and $25.1 \times 21.7 \text{ \AA}^2$ for SL-MoS₂ surfaces. Brillouin zone sampling of the total energy was based on the technique by Monkhorst and Pack²⁶ with a k-point mesh of $3 \times 3 \times 1$, increased to $6 \times 6 \times 1$ for LDOS and charge transfer calculations. A k-point mesh of $5 \times 5 \times 1$ was used for structural optimization and total energy calculations for the MoS₂ and graphene surfaces on SiO₂ with a smaller cell, increased to $10 \times 10 \times 1$ for LDOS and charge calculations. A k-point mesh of $3 \times 3 \times 1$ for 2,4,6-trinitrotoluene on MoS₂ and graphene surfaces on SiO₂ was used because a larger cell was required. In calculation of the total energy of the system for a relaxed configuration, all atoms in a supercell were allowed to move in all directions and the structure was relaxed until the forces acting on each atom were converged to less than 0.01 eV/\AA . Bader charge analyses²⁷ were used to analyze charge transfer.

III. RESULTS AND DISCUSSION

A. Physisorption on free-standing graphene and MoS₂ surfaces

First, we describe details of adsorption on graphene and MoS₂ surfaces. The graphene surface structure is shown in

Fig. 1(a), having C-C bond lengths of 1.42 \AA . MoS₂ has a closely packed layered structure with each Mo atom coordinated by six sulfur atoms in a trigonal prismatic unit, with Mo-S bond lengths of 2.40 \AA (Fig. 1(b), side views Figs. 1(c) and 1(d)). Mo atoms in a plane between two planes are in 2-H stacking,²⁸ with S at a perpendicular distance of 3.16 \AA . For each of the molecular adsorbates, namely, triethylamine, acetone, tetrahydrofuran methanol, 2,4,6-trinitrotoluene, o-nitrotoluene, o-dichlorobenzene, and 1,5-dichloropentane, various adsorption sites were examined, as described below. The adsorption energy E_{ads} was derived by subtracting the total energy of any given molecule E_{mol} and that of the corresponding fully relaxed unadsorbed MoS₂ or graphene surface system E_{surf} from the total energy of the hybrid material system, namely, $(E_{mol/surf})$: $E_{ads} = E_{mol/surf} - E_{surf} - E_{mol}$.

Because the PBE functional does not account for London dispersion upon physisorption, the reported geometries and adsorption energies were calculated using the vdW-DF²⁵ non-empirical correction to the GGA functional, previously shown, for example, to be important for peptide aromatic residue adsorption.¹⁶ Results using PBE with the vdW-DF correction indeed demonstrate a stronger relative adsorption, e.g., for 2,4,6-trinitrotoluene, as expected, as summarized in Table I. The optimized structures are depicted in Fig. 2. Distances of heavy atoms in the molecular moiety to the adsorbing surface are listed in Table II. Because the chemical structures are physisorbed on the surfaces we note that in all cases the internal structure of the molecule has been hardly perturbed.

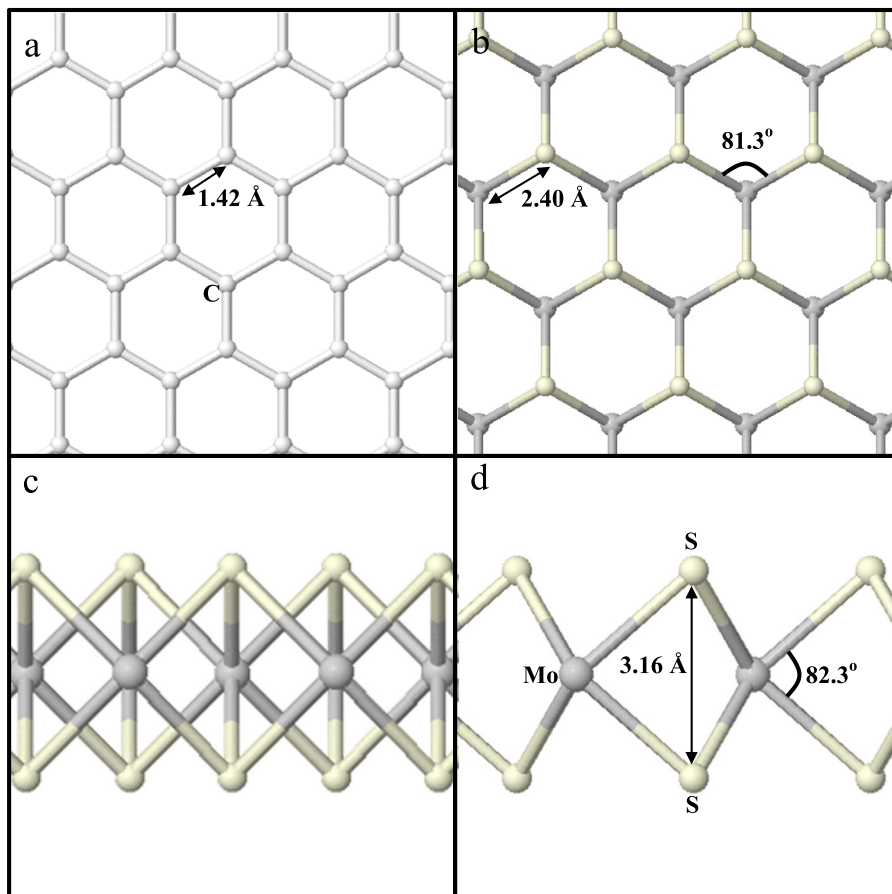


FIG. 1. The minimum energy structures of (a) graphene, (b)-(d) MoS₂ with two side views (c) and (d).

TABLE I. Adsorption energies (eV) of molecules on preferred adsorption sites (structures shown in Fig. 2), calculated with PBE and the vdW-DF non-empirical correction to the PBE functional.

	Graphene		MoS ₂	
	PBE	PBE, vdW-corrected	PBE	PBE, vdW-corrected
Triethylamine	-0.05	-0.34	-0.08	-0.40
Acetone	-0.04	-0.26	-0.02	-0.26
Tetrahydrofuran	-0.05	-0.30	-0.03	-0.31
Methanol	-0.04	-0.14	-0.04	-0.16
2,4,6-trinitrotoluene	-0.10	-0.59	-0.05	-0.57
o-nitrotoluene	-0.06	-0.42	-0.04	-0.40
o-dichlorobenzene	-0.04	-0.37	-0.02	-0.37
1,5-dichloropentane	-0.01	-0.46	-0.02	-0.48

Two sites for adsorption for triethylamine on graphene were analyzed, with the nitrogen atom in both starting configurations on top of graphene's carbon atom, but in one case the nitrogen and ethyl groups bent inwards and in the other outwards. The inward structure was slightly lower in energy, with a binding energy of -0.34 eV (Table I) as compared to -0.30 eV for outward adsorption. The molecule was displaced from its starting position, with the nitrogen atom moving from the (0, 0) top site to a position in the xy-plane ($-0.34, 0.23$ Å) (see structure in Fig. 2(a)). On MoS₂, the site with the nitrogen atom and ethyl groups of triethylamine pointing outwards was preferred by 0.03 eV. The molecule undergoes significant motion and was transferred from an initial position on top of a sulfur atom to a hollow site (Fig. 2(b)). Optimized distances of the nitrogen atom to the surfaces are somewhat shorter for graphene as compared to MoS₂ (4.44 Å vs. 4.63 Å, respectively, in Table II). Stronger adsorption is noted on the MoS₂ surface, of -0.40 eV.

In adsorption of acetone, investigated for five nonequivalent sites, a different behavior for the two surfaces is shown. Adsorption sites considered included the oxygen atom positioned on the top, bridge and hollow sites and central CO parallel to the surface, and in another case the oxygen atom pointed away from the surface. The preferable adsorption site on the graphene surface (so-called CO-flat, shown in Fig. 2(a)) resulted in a binding energy of -0.26 eV (Table I), while a top site with adsorption energy of -0.19 eV was the next strongest adsorbed structure. In this case, the CO bond is no longer parallel to the surface, but the O atom is slightly tilted toward the graphene C atom at a distance of 5.96 Å (Table II). Similarly, the CO bonds of acetone on the top, bridge and hollow sites do not stay perpendicular to the graphene surface upon relaxation but are tilted with a slightly smaller angle than the most preferred site (CO-flat). On MoS₂, the on-top site is slightly preferred by 0.03 eV, as compared to the CO-flat site. Examination of the structures indicated small differences between the two sites, with an O-S bond distance (d_{O-S}) of 0.14 Å, which is smaller than for the most preferred adsorption site. Fig. 2(b) shows the minimum energy structure, and the corresponding distance (Table II) demonstrates closer proximity to the surface than for

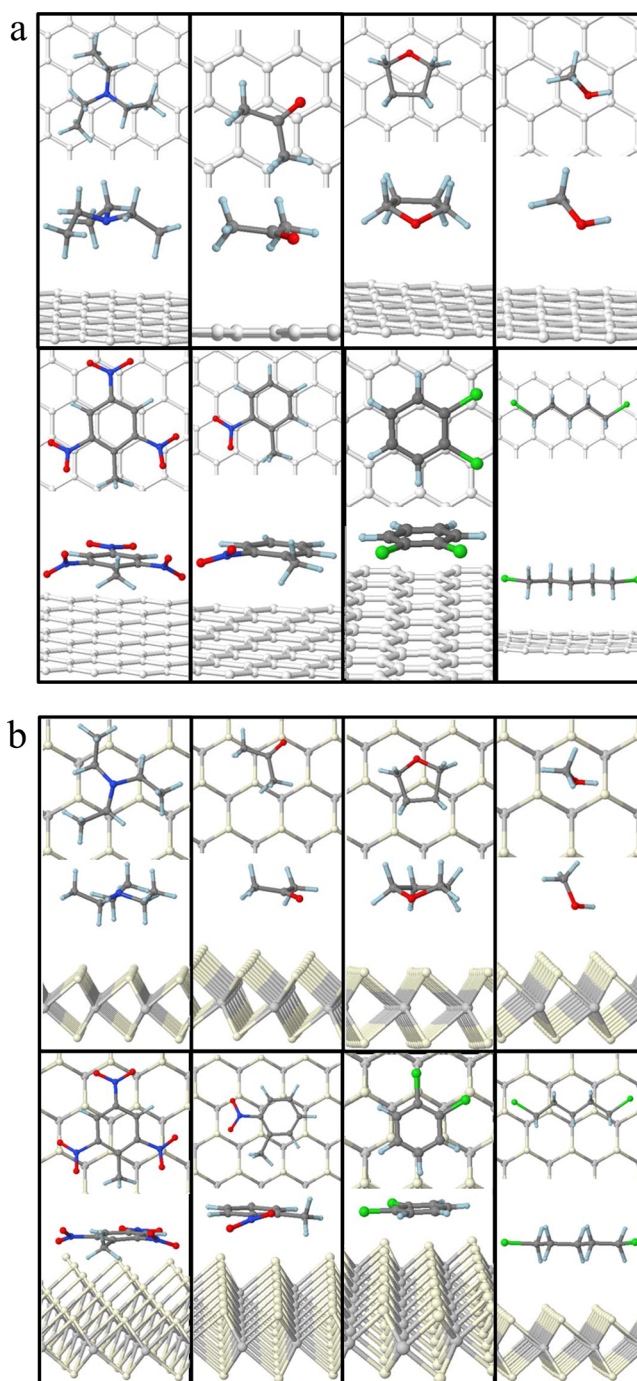


FIG. 2. Top and side views of adsorbed triethylamine, acetone, tetrahydrofuran, methanol (left to right top panel) and 2,4,6-trinitrotoluene, o-nitrotoluene, o-dichlorobenzene and 1,5-dichloropentane (bottom panel left to right, respectively) on (a) graphene and (b) MoS₂ surfaces.

graphene. The adsorption energies for the remaining three sites were in the range of -0.13 – -0.16 eV.

For tetrahydrofuran, with out-of-plane oxygen atom in the ring structure, we considered four distinct sites for adsorption. Two sites consider adsorption in a perpendicular direction through the oxygen atom on top and hollow sites on the surface, while the remaining two sites consider planar adsorption parallel to the surface with the center of the tetrahydrofuran ring aligned with the graphene ring (planar-top site) and the center of the tetrahydrofuran on top of the C

TABLE III. Accumulation (+) and depletion (−) of charge (e) for molecular adsorbates on free-standing graphene and MoS₂ surfaces.

	Graphene	MoS ₂
Triethylamine	−0.003 (−0.128) ^a	−0.001 (−0.250) ^a
Acetone	0.005 (0.037) ^a	−0.039 (−0.147) ^a
Tetrahydrofuran	0.002	−0.021
Methanol	−0.001	0.002
2,4,6-trinitrotoluene	0.140 (0.017) ^a	0.038 (0.031) ^a
o-nitrotoluene	0.006	0.009
o-dichlorobenzene	−0.001	0.037
1,5-dichloropentane	0.005	0.012

^aResults for SiO₂-supported graphene and MoS₂ surfaces.

to the surface (−0.43 eV). This implies a stronger binding energy with a larger number of alignment of the bonds. We found this to hold for the MoS₂ surface too. A slightly stronger bound 1,5-dichloropentane (by ~0.02 eV) stayed relatively far from the MoS₂ surface with a S–C bond length (d_{S-C}) of 4.00 Å, as compared to a graphene–C distance (d_{G-C}) of 3.40 Å (Table II).

B. Charge transfer upon chemical adsorption

Comparing changes in charge transfer upon molecular adsorption to the relative conductivity change of a nano-FET is complicated because of consideration of only one molecule in the calculations, and lack of consideration of impurities or defects.^{16,23} However, in this work, we seek an intrinsic response of the surface to molecular adsorption. Bader charge analyses are summarized in Table III. Charge transfer on free-standing surfaces demonstrate small changes, of 0.00–0.04 e except for 2,4,6-trinitrotoluene, consistent with physisorbed adsorbates in other work.¹⁴ Note that, for example, for triethylamine and acetone, these small values are consistent with the corresponding distances of the nitrogen and oxygen atoms to the surfaces, respectively (Table II). Triethylamine and acetone had no noticeable effect on shifting the Dirac point away from the Fermi level in the LDOS for the graphene surface because of the minimal charge transfer (Fig. 3). Results for the MoS₂ surface for triethylamine and acetone similarly show a small response (Figs. 4(a) and 4(b)). On the other hand, charge transfer to 2,4,6-trinitrotoluene was calculated to be somewhat larger than for other adsorbates (Table III), as expected. The removal of charge from the graphene surface upon adsorption of the strong electron-acceptor will consequently shift the Dirac point in LDOS away from the Fermi level towards higher energies (conduction band), as shown in Fig. 3, while the LDOS of MoS₂ in Fig. 4 also show a small shift around the Fermi level.

Experimentally, however, robust sensitivity was indicated for triethylamine, a laboratory-safe decomposition product from the V-series of nerve gas agents, and also acetone, particularly for MoS₂.¹² To explore potential interactions with the underlying SiO₂ substrate that may explain this behavior, charge transfer for surfaces on silica was considered for selected cases. A model based on α -quartz was considered, because it represents the local character of SiO₂'s amorphous structure,³⁰ as previously rationalized.³¹ It

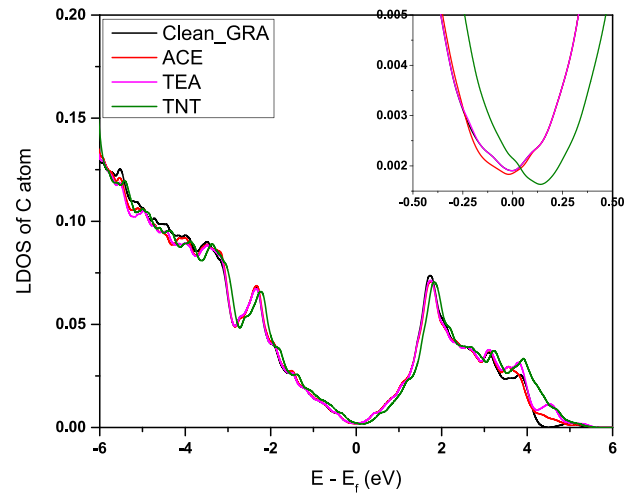


FIG. 3. LDOS of carbon atom for free-standing graphene (black line) compared with carbon atom of graphene with adsorbed TEA, ACE, and TNT. Inset shows the enlarged version of Dirac point shift for supported graphene.

was shown that differences in adsorption of graphene on a SiO₂ substrate based on α -quartz or cristobalite models are small,³⁰ and because our goal was to understand relative changes upon molecular adsorption, only one type of surface was evaluated. It was pointed out³¹ that experimental and theoretical studies showed that the upper subsurfaces of cleaved SiO₂ undergo surface reconstruction that results in

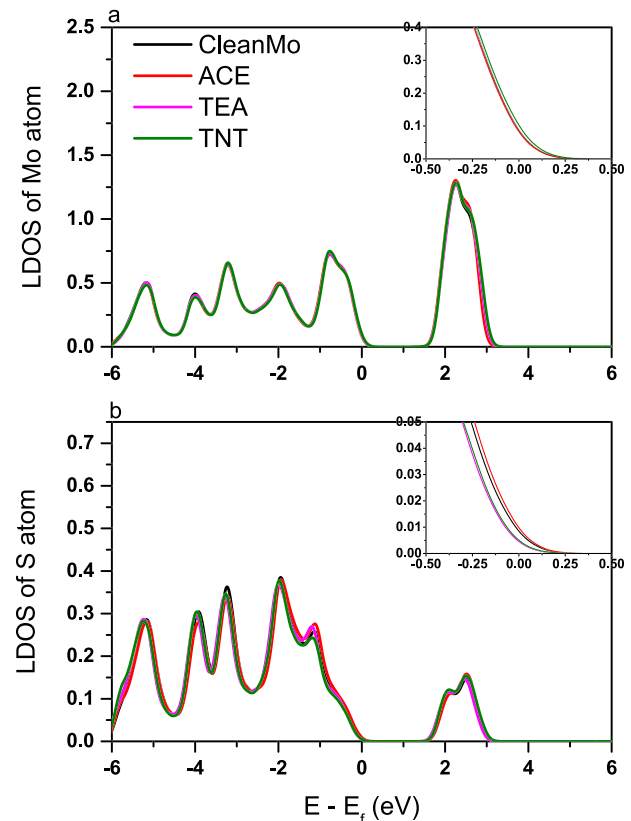


FIG. 4. LDOS of (a) Mo atom and (b) S atom of free-standing MoS₂ surface (black line) compared with Mo atom of MoS₂-surface with an adsorbed TNT molecule. Insets show the enlarged version of the plot around Fermi energy showing a shift in the LDOS.

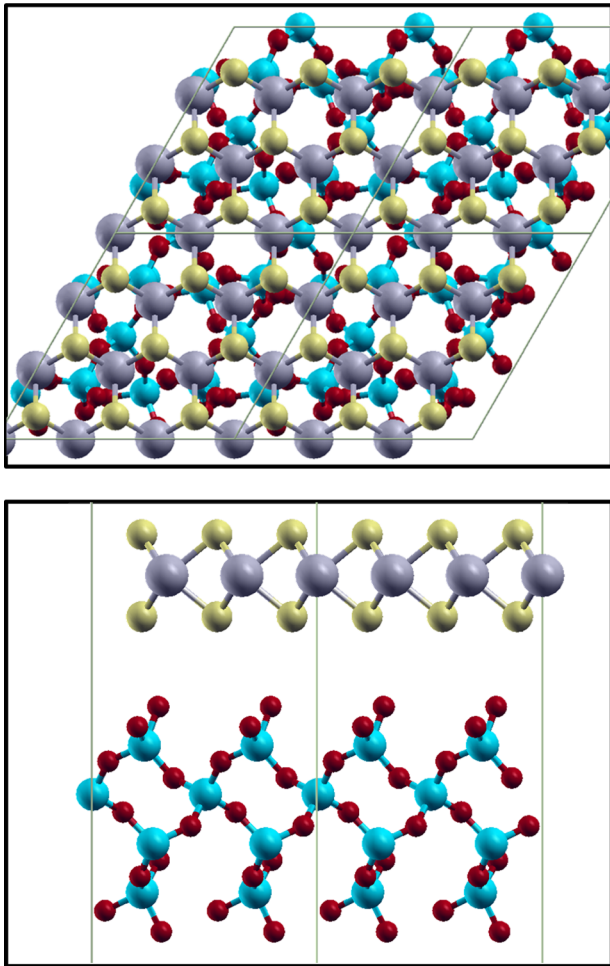


FIG. 5. A top (a) and side view (b) of MoS₂ on SiO₂ substrate.

oxygen-terminated surfaces.³² It was also shown that the optimized structures of graphene on oxygen-terminated or hydroxylated (0001) SiO₂ surfaces are similar.³¹ We note

that comparing to an experimental *n*-type device,¹² presumably due to defects and impurities as shown in recent theoretical work,¹⁵ it is unlikely that there are silanol groups on the SiO₂ surface. We therefore considered an oxygen-terminated α -quartz SiO₂ surface.

The choice to model the substrate by a (0001) α -quartz surface was additionally based on the small lattice mismatch for both MoS₂ and graphene surfaces. The optimized structure of the α -quartz SiO₂ model structure resulted in Si-O bond lengths between 1.62–1.65 Å with a Si-O-Si bond angle of 142.6°, in agreement with earlier calculations.³⁰ The calculated lattice constant for graphene was 2.46 Å, and therefore, a 4 × 4 cell of graphene (32 C atoms) was adsorbed on a 2 × 2 cell of (0001) SiO₂, leading to a lattice mismatch of ~3%. A 2 × 2 cell with four layers of α -quartz SiO₂ terminated with oxygen was modeled with a vacuum region of 20 Å. The lattice parameter of α -quartz SiO₂ was calculated as 4.85 Å and for MoS₂ was 3.20 Å. A 3 × 3 cell of MoS₂ (9 Mo and 18 S atoms) was therefore adsorbed on a 2 × 2 cell of (0001) SiO₂ (16 Si and 40 O atoms), leading to a lattice mismatch of ~2%. The small strain was shown not to affect the electronic properties.¹⁵ For computational feasibility, the cell size was reduced by almost a half from what we used for the unsupported graphene and MoS₂ surfaces. Optimized distances between the top layer of SiO₂ and the adsorbed surfaces were 2.85 Å for graphene and 2.97 Å for MoS₂ (shown in Fig. 5 for MoS₂). Charge densities for graphene and MoS₂ on SiO₂ are shown in Figs. 6(a) and 6(b), respectively.

The SiO₂ substrate causes *p*-doping by 1.071 e and 0.738 e of graphene and MoS₂ surfaces, respectively. As a consequence of the graphene *p*-doping, which is consistent with results for cristobalite SiO₂,¹⁴ the Dirac point of the LDOS is shifted from valence band towards the higher energies (conduction band) by 1.15 eV, as shown in Fig. 7. The LDOS of Mo and S atoms for the MoS₂ surface on SiO₂ are shown in Figs. 8(a) and 8(b), demonstrating a shift of the band gap of

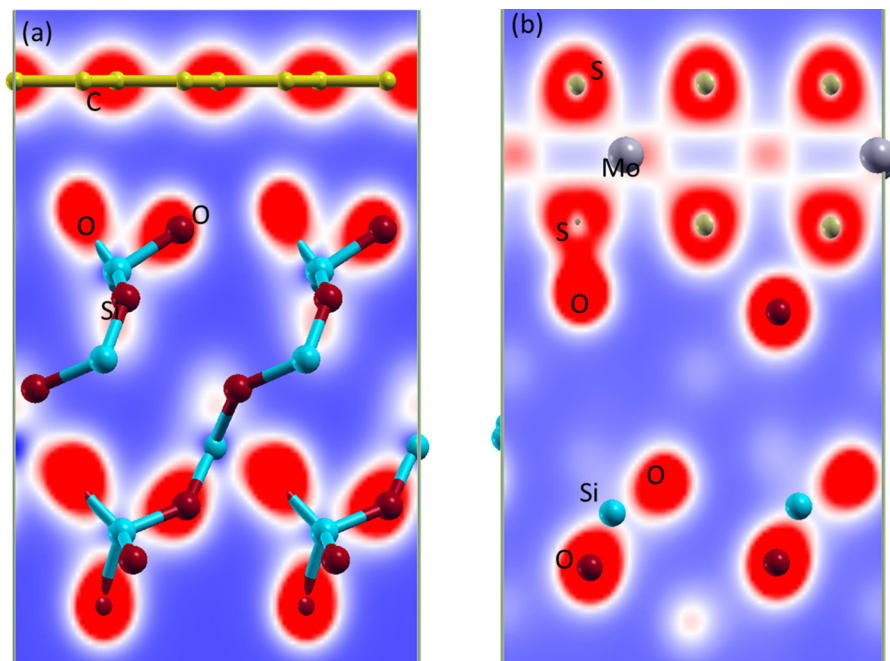


FIG. 6. Surface contour plots of charge densities for graphene and MoS₂ adsorbed on SiO₂ plotted along a plane passing through the center of (a) carbon of graphene, silicon, and oxygen atoms and (b) molybdenum, sulfur, silicon, and oxygen atoms.

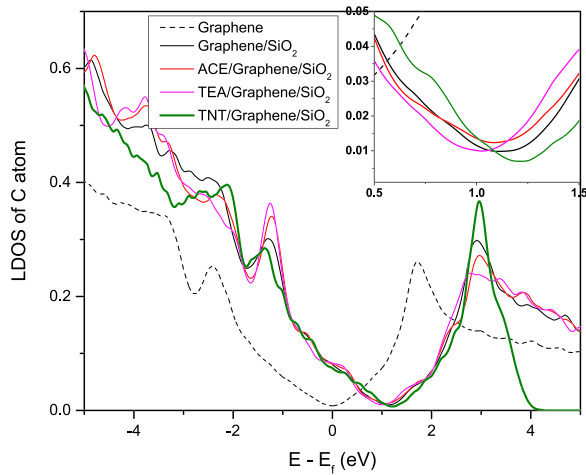


FIG. 7. LDOS of carbon atom of free-standing graphene (dashed black line) and supported graphene (solid black line) with TEA and ACE. Inset shows the enlarged version of Dirac point shift.

about 0.25 eV, consistent with the charge transfer. This response affects, in turn, changes in charge transfer upon molecular adsorption, for example, the electron-accepting 2,4,6-trinitrotoluene molecule shows accumulation of charge on free-standing surfaces of graphene and MoS₂. Charge transfer, however, to graphene and MoS₂ surface with the SiO₂ substrate is smaller, because of the *p*-doping of the surfaces, as expected.

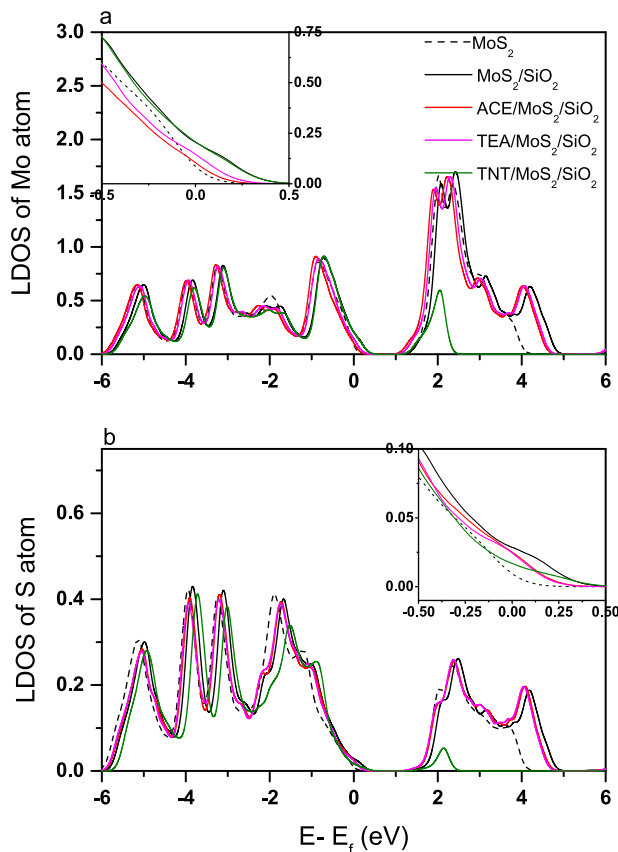


FIG. 8. LDOS of Mo atom (a) and sulfur atom (b) for free-standing MoS₂ (dashed line) and supported MoS₂ with adsorbed TEA and ACE. Inset shows the enlarged version of LDOS around Fermi-level.

On the other hand, depletion of charge on triethylamine for adsorption on both graphene and MoS₂ surfaces modeled on a substrate is noted, of 0.128 e and 0.250 e, respectively (see Table III), as well as for acetone on MoS₂ (e.g., 0.147 e on MoS₂, Table III, however, inconclusive for graphene). Interestingly, the intrinsic effect is stronger for MoS₂, qualitatively consistent with experimental observations.¹² A smaller Dirac point shift because of a smaller charge transfer for the system with the triethylamine and acetone on graphene is noted in Fig. 7. Because triethylamine and acetone *n*-dope the SiO₂-supported MoS₂ surface more significantly, the LDOS shift towards the valence band (lower energies) upon triethylamine adsorption (Fig. 8) is more noticeable compared to graphene.

IV. CONCLUSIONS

In this work, we investigated by DFT calculations the physisorption of the molecular adsorbates triethylamine, acetone, tetrahydrofuran, methanol, 2,4,6-trinitrotoluene, o-nitrotoluene, o-dichlorobenzene, and 1,5-dichloropentane on surfaces of single-layer MoS₂ and graphene, in order to understand parameters that may affect the intrinsic response for chemical sensing application. Detailed investigation of adsorption sites for the hybrid material systems, and correction for London dispersion in the DFT functional, assured accuracy of the calculated adsorption energies. Charge transfer analyses and LDOS results for the optimized surface with chemical adsorbates demonstrated very small effects. However, inclusion of an underlying SiO₂ substrate model surfaces in some cases, provided rationalization of the observed sensing for triethylamine, for example. These results may assist in devising chemical sensors for improved sensitivity.

ACKNOWLEDGMENTS

Support for this work was provided by the Air Force Office of Scientific Research through a National Research Council (NRC) postdoctoral fellowship. The AFRL DoD Supercomputing Resource Center is acknowledged for providing computational resources and helpful support.

- ¹S. Z. Butler *et al.*, *ACS Nano* **7**, 2898 (2013).
- ²Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* **7**, 699 (2012).
- ³D. Jariwala, V. K. Sangwan, D. J. Late, J. E. Johns, V. P. Dravid, T. J. Marks, L. J. Lauhon, and M. C. Hersam, *Appl. Phys. Lett.* **102**, 173107 (2013).
- ⁴N. R. Pradhan, D. Rhodes, Q. Zhang, S. Talapatra, M. Terrones, P. M. Ajayan, and L. Balicas, *Appl. Phys. Lett.* **102**, 123105 (2013).
- ⁵S. Das, H.-Y. Chen, A. V. Penumatcha, and J. Appenzeller, *Nano Lett.* **13**, 100 (2013).
- ⁶B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nat. Nanotechnol.* **6**, 147 (2011).
- ⁷S. Ghatak, A. N. Pal, and A. Ghosh, *ACS Nano* **5**, 7707 (2011).
- ⁸V. K. Sangwan, H. N. Arnold, D. Jariwala, T. J. Marks, L. J. Lauhon, and M. C. Hersam, *Nano Lett.* **13**, 4351 (2013).
- ⁹H. Li *et al.*, *Small* **8**, 63 (2012).
- ¹⁰Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang, and H. Zhang, *Small* **8**, 2994 (2012).
- ¹¹D. J. Late *et al.*, *ACS Nano* **7**, 4879 (2013).
- ¹²F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, and B. T. Jonker, *Nano Lett.* **13**, 668 (2013).

- ¹³Z. Yin *et al.*, *ACS Nano* **6**, 74 (2012).
- ¹⁴B. Kumar *et al.*, *Nano Lett.* **13**, 1962 (2013).
- ¹⁵K. Dolui, I. Rungger, and S. Sanvito, *Phys. Rev. B* **87**, 165402 (2013).
- ¹⁶B. Akdim, R. Pachter, S. S. Kim, R. R. Naik, T. R. Walsh, S. Trohalaki, G. Hong, Z. Kuang, and B. L. Farmer, *ACS Appl. Mater. Interfaces* **5**, 7470 (2013).
- ¹⁷Y.-Y. Chen, M. Dong, Z. Qin, X.-D. Wen, W. Fan, and J. Wang, *J. Mol. Catal. A: Chem.* **338**, 44 (2011).
- ¹⁸P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ²⁰G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ²¹G. Kresse and J. Hafner, *Surf. Sci.* **459**, 287 (2000).
- ²²G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ²³F. Mehmood, R. Pachter, W. Lu, and J. J. Boeckl, *J. Phys. Chem. C* **117**, 10366 (2013).
- ²⁴J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁵M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004).
- ²⁶H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ²⁷R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, New York, 1990).
- ²⁸M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, *Nat. Chem.* **5**, 263 (2013).
- ²⁹S. B. Fagan, E. C. Girão, J. M. Filho, and A. G. S. Filho, *Int. J. Quantum Chem.* **106**, 2558 (2006).
- ³⁰X. F. Fan, W. T. Zheng, V. Chihaiia, Z. X. Shen, and J.-L. Kuo, *J. Phys.: Condens. Matter* **24**, 305004 (2012).
- ³¹T. C. Nguyen, M. Otani, and S. Okada, *Phys. Rev. Lett.* **106**, 106801 (2011).
- ³²G. M. Rignanese, V. A. De, J. C. Charlier, X. Gonze, and R. Car, *Phys. Rev. B: Condens. Matter Mater. Phys.* **61**, 13250 (2000).