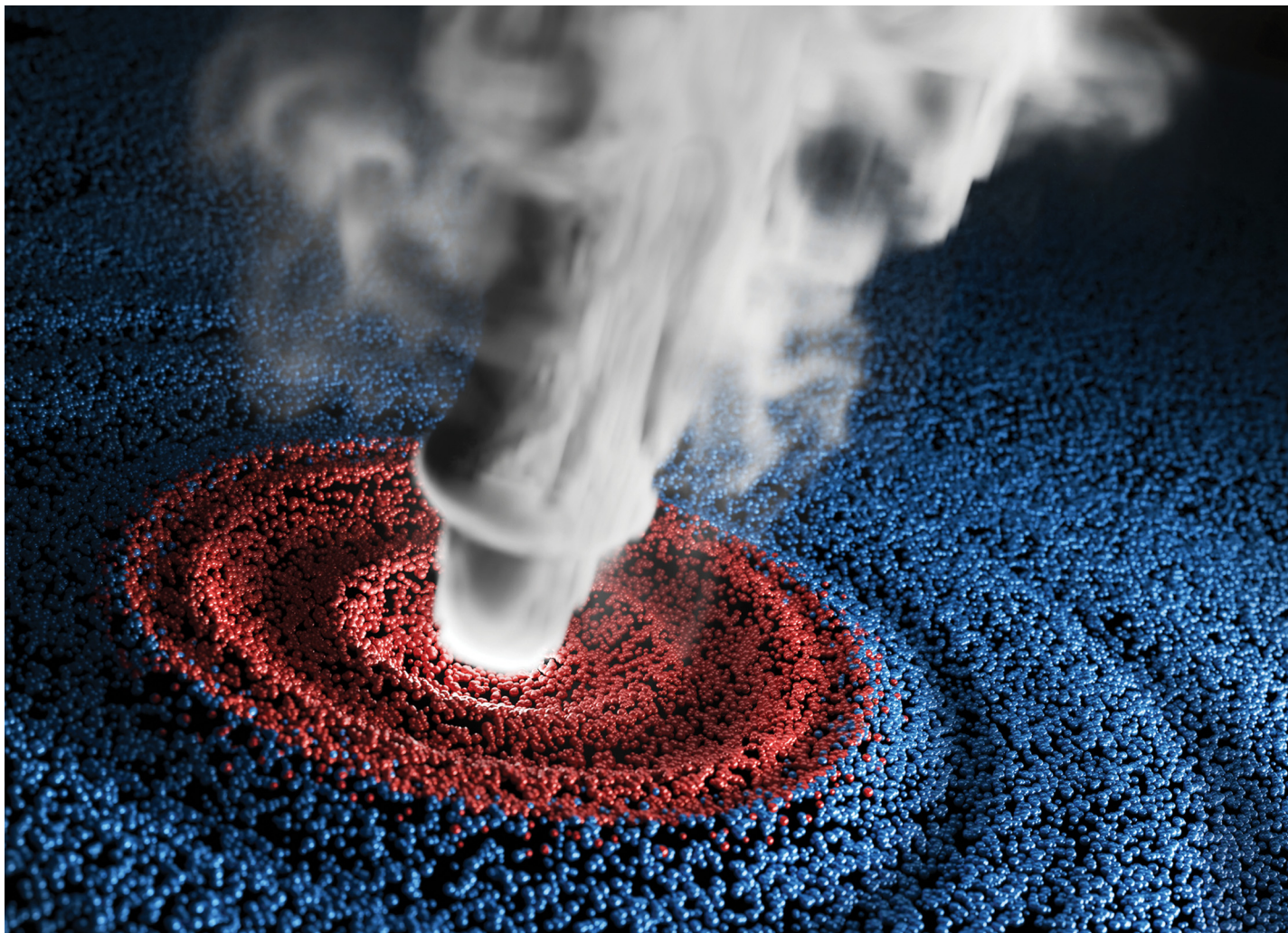




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Interaction of nitrogen mustard agents and their simulant with zinc oxide surfaces: a density functional theory study

Understanding how toxic molecules interact with oxide surfaces is essential for the development of next-generation chemical sensors. This study combines advanced quantum-chemical calculations to uncover the adsorption mechanisms of a nitrogen mustard agent and its simulant on ZnO. The results reveal remarkably similar electronic responses despite the distinct molecular structures of the two molecules and identify oxygen-induced conductivity-type switching as a key feature governing the sensing behaviour of ZnO surfaces.

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Cite this: *Phys. Chem. Chem. Phys.*,
2026, **28**, 20019

Interaction of nitrogen mustard agents and their simulant with zinc oxide surfaces: a density functional theory study

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The interaction of hazardous chemical warfare agents (CWAs) with metal oxide surfaces is relevant for understanding their detection by chemiresistive sensors. In this work, the adsorption behaviour of a nitrogen mustard (HN2) and its simulant, dipropylene glycol monomethyl ether (DPGME), on stoichiometric and oxygen-enriched ZnO surfaces is investigated using density functional theory-based methods, complemented by higher-level calculations on the isolated molecules. Both molecules adsorb via coordination to exposed Zn sites and exhibit comparable adsorption energies across all surface models. Despite their distinct molecular structures, HN2 and DPGME induce closely similar modifications in the electronic structure of ZnO, as evidenced by charge transfer analysis, density of states, and work function variations. Oxygen enrichment significantly alters the electronic properties of the surface, leading to a transition from an n-type to a p-type character, which is reversed upon molecular adsorption. Multiple analyses consistently support adsorption-induced electronic redistribution. These results provide atomistic insight into the relationship between adsorption geometry, charge redistribution, and electronic response at oxide surfaces, and rationalize the similar behaviour of structurally different molecules at the ZnO interface.

Received 4th May 2026,
Accepted 29th June 2026

DOI: 10.1039/d6cp01648k

rsc.li/pccp

Introduction

Chemical Warfare Agents (CWAs) are a severe hazard for both human health and the environment due to their colorless, odorless, and toxic characteristics.^{1–6} Although their military use is globally banned by international regulations,^{2,4,7–10} these gases can still display deadly potential in terrorist attacks, making them a persistent threat in the 21st century.¹¹ For this reason, the development of efficient sensing devices for CWAs is unquestionably of strategic relevance for safety applications.^{12–16} In particular, effective detection of CWAs can be achieved through chemiresistive sensors.¹⁷ These devices can detect the change in sensor resistance when the sensing material interacts with the analytes. Indeed, chemiresistive gas sensors based on nanostructured metal oxides have attracted considerable attention due to their low cost, limited power consumption, and good stability and sensitivity.¹⁷

Within this class, zinc oxide (ZnO), commonly considered as an n-type semiconductor, is a particularly appealing candidate: it is a biocompatible, chemically stable, and inexpensive wide-band gap material ($E_G = 3.37$ eV), and it has already been widely

applied for the detection of toxic gases.^{17–22} In this context, ZnO nanosystems have shown remarkable gas sensing ability, in view of the considerable variations in sensor resistance when gas molecules interact with their surfaces.²³ According to a widely accepted picture, oxygen molecules are adsorbed on ZnO surfaces.^{24–26} Such adsorbed oxygen species drain electrons from the ZnO conduction band (CB) and may convert to ionized forms upon increasing temperature.²³ In an n-type semiconductor like ZnO, this process generates the so-called “surface depletion layer”, which is deemed responsible for a measurable increase of the resistance upon exposure to air. Upon contact of the ZnO material surface with reductive gases – such as most CWAs are – the electrons captured by the surface are re-injected into the ZnO CB, thus leading to a significant decrease in the sensor resistance.^{21,27} Nonetheless, “emerging experimental evidence has revealed an intriguing n–p/p–n conductivity-type transition phenomenon during gas sensing processes, which has stimulated intense scientific discussion within the sensor community.”²⁸ Such an intriguing phenomenon, which has been observed for several semiconductor oxides, has been ascribed to a variety of origins (*e.g.* temperature conditions, concentration of dopants, type/concentration of defects, *etc.*), but it is still not fully understood.²⁸ In particular, in the case of ZnO,^{29–33} this kind of behaviour, which typically emerges as a consequence of different annealing treatments, might be associated with excess oxygen

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species on the exposed surfaces.^{31,33} Specifically, it has been found that n-type ZnO sensors have much lower oxygen to zinc ratios than p-type ZnO ones.^{31,33}

Previous experimental studies have demonstrated the feasibility of using ZnO-based chemiresistive sensors for the indirect detection of CWAs through simulants. For instance, ZnO nanostructures have shown measurable responses to dimethyl methylphosphonate (DMMP), a well-established simulant for nerve agents such as sarin.^{34,35} Furthermore, the integration of ZnO-based materials into portable sensing devices is relatively simple, opening the way to a variety of end-uses.²¹ Despite this progress, a detailed understanding of the fundamental interactions between CWAs and ZnO surfaces remains limited.

In this scenario, it is worth underlining that real CWAs are extremely hazardous compounds and require exceptional care, as well as specific dedicated infrastructure,³⁶ for their storage, manipulation, and environmentally friendly disposal. Hence, only a few laboratories worldwide are allowed to directly handle these substances. Accordingly, research activities aimed at CWA detection are conducted on less toxic molecules denoted as surrogates, or simulants, which mimic the properties of the target CWA but conform to the security regulations of common laboratories. These compounds are of key relevance in experimental research on CWAs, providing a secure yet effective route for implementing new detection methods, or enhancing the functionalities of existing sensors. However, the relationships between the simulant compounds and the actual CWAs are not fully understood at the atomistic level. For this reason, computational investigations aimed at finding correlations between true CWAs and their simulants are becoming increasingly important in this context,^{37–43} underlying thus “the importance of thinking on the molecular/atomic level”.¹ In particular, density functional theory (DFT) calculations provide a microscopic viewpoint on the geometry, electronic structure, and adsorption energies of these substances.^{37,38,44,45} Unfortunately, DFT studies aimed at unraveling the electronic and adsorption behavior of these species on ZnO are still scarce.

Among the different CWA categories, blistering agents, or vesicants, mainly cause acute skin blisters. These CWAs usually act as alkylating agents, causing DNA damage as well as severe inflammatory effects on the skin, eyes, and respiratory tract.^{2,3} Such substances are extremely toxic and potentially lethal. Besides sulfur mustard gas, this category also includes the azoyprites, or nitrogen mustards, traditionally denoted as HN1, HN2, and HN3.^{2,3} Indeed, these three molecules – namely HN1 (bis(2-chloroethyl)-ethylamine, $C_6H_{13}Cl_2N$), HN2 (bis(2-chloroethyl)-methylamine, $C_5H_{11}Cl_2N$), HN3 (tris(2-chloroethyl)amine, $C_6H_{12}Cl_3N$) – present similar molecular structures and physicochemical properties, as well as analogous vesicant effects. In general, simulants are characterized by very similar chemical structural features compared to real CWAs. However, the nitrogen mustard simulant – namely, DPGME (dipropylene glycol monomethyl ether, $C_7H_{16}O_3$) – is characterized by a markedly different molecular structure, exhibiting functional groups apparently unrelated to azoyprites’ characteristic ones. Nonetheless, various studies in the literature document DPGME as a good surrogate for this class of CWAs.^{17,46} Indeed,

responses to DPGME as a mustard gas simulant have been reported on graphene oxide,⁴⁷ Mn_3O_4 -based nanostructures,^{46,48} MnO_2 nanocomposites with CuO/SnO_2 ,⁴⁹ ZnO-doped SnO_2 ,⁵⁰ as well as on other SnO-based sensing devices.⁵¹

In this work, we employ computational methods to establish atomistic-scale relationships between the structural and electronic properties of nitrogen mustard chemical warfare agents and those of their commonly used simulant, DPGME. After analysing the isolated molecules using hybrid DFT and MP2 approaches, periodic DFT calculations are performed to investigate the adsorption behaviour of CWA and simulant on both stoichiometric and oxygen-enriched $ZnO(10\bar{1}0)$ surfaces. For computational convenience, among the nitrogen mustards (HN1–HN3), the smallest HN2 molecule was selected as the representative of this class of CWAs in view of the close similarity of their functional groups. Therefore, all adsorption studies were performed with HN2 and DPGME.

By comparing the structural, electronic, and adsorption properties of the agent and its simulant, this study aims to provide a molecular-level rationale for the use of DPGME as a surrogate for nitrogen mustard agents, while also offering insight into the relationship between adsorption-induced charge redistribution and the resulting electronic response of the ZnO surface.

Computational methods and models

Isolated molecules

The molecular structures of the four target molecules – *i.e.*, the three azoyprites (HN1, HN2, and HN3) and their simulant DPGME – were optimized in a vacuum, employing DFT with the ω B97XD exchange–correlation functional, which includes an empirical dispersion correction.⁵² Geometry optimizations were carried out using the 6-311+G(d,p) basis set. Starting from the DFT optimized structures of the target molecules, geometry optimizations at the MP2/6-311+G(d,p) level were carried out as well. All optimized DFT and MP2 structures are characterized by no imaginary frequencies. All calculations on the isolated molecules were performed with the Gaussian09 package.⁵³

Adsorption on the $ZnO(10\bar{1}0)$ slab models

The ZnO primitive cell has a wurtzite-type crystal structure, with hexagonal symmetry. The initial values for the lattice parameters $a = b = 3.1590$ Å and $c = 5.0796$ Å were taken from the literature.⁵⁴ To model adsorption of HN2 and DPGME on ZnO, we selected the non-polar $(10\bar{1}0)$ surface, the thermodynamically most stable termination of ZnO materials.⁵⁵ A slab model $(10\bar{1}0)$ surface was derived from the bulk ZnO structure, its a and b parameters were optimized, and convergence with respect to the number of layers was tested (see SI, Table S1).

The stoichiometry of the final $ZnO(10\bar{1}0)$ slab model adopted in this work is $Zn_{54}O_{54}$, with an exposed surface area of 151.3 Å². As aforementioned, this surface is non-polar since it exposes both Zn and O atoms. The adopted slab model is constituted by three ZnO bilayers. A vacuum space of 16.9 Å was added on top of the surface to reduce inter-slab interactions

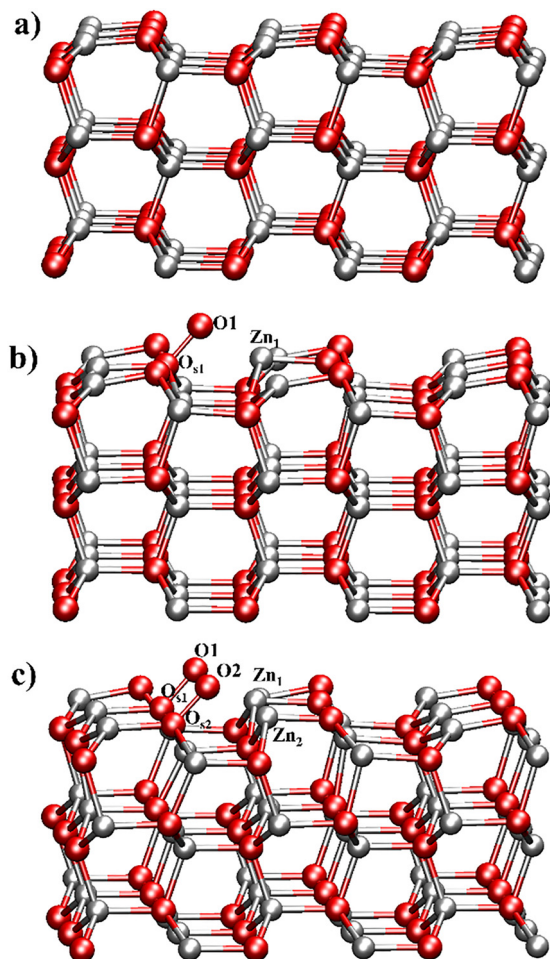


Fig. 1 Optimized slab models for: (a) stoichiometric ZnO(1010); (b) ZnO(1010) with one adsorbed O atom (ZnO + O); and (c) ZnO(1010) with chemisorbed O₂ (ZnO + 2O). Color codes: gray = Zn; red = O.

along the *z* direction and to prevent significant wavefunction overlap among replicas. The final optimized simulation cell parameters were $a = 15.5945$ Å, $b = 9.7011$ Å, and $c = 23.4740$ Å. While the atoms belonging to the bottom bilayer were kept fixed during geometry optimizations, all other atoms were allowed to relax until a convergence of 1.0×10^{-4} Rydberg per Bohr for the forces on the nuclei was reached (1.0×10^{-7} Rydberg for the energy convergence).

In addition to the regular stoichiometric slab (Fig. 1a), two oxygen-enriched slab models were considered, featuring additional oxygen adatoms. Specifically, the first model – denoted as ZnO + O – features an oxygen adatom adsorbed on the top layer of the ZnO(1010) slab (Fig. 1b), while the second one – denoted as ZnO + 2O – mimics the dissociative adsorption of an oxygen molecule on the ZnO(1010) top layer (Fig. 1c).

These models were adopted to investigate how the presence of surface oxygen adatoms affects adsorption energetics, charge redistribution, and electronic properties at the interface. Geometry optimization of these slab models was performed using the same computational protocol adopted for the optimization of the regular ZnO(1010) model. These oxygen-enriched ZnO(1010) surfaces were

modelled by introducing oxygen species on one side of the slab, leading to asymmetric surface models. This approach is widely adopted in periodic DFT investigations of defective and adsorbate-covered oxide surfaces and enables a direct comparison of the effects of increasing oxygen coverage on adsorption and electronic properties.⁵⁶ Surface polarization effects associated with slab asymmetry were not explicitly corrected in the present calculations. Nevertheless, all systems were investigated using the same vacuum thickness and computational setup. Therefore, possible systematic contributions arising from slab asymmetry are expected to affect all models in a similar manner, allowing meaningful comparison of the calculated energetic and electronic trends across the investigated systems.

To investigate CWA adsorption on regular and oxygen-enriched ZnO(1010) slab models, only the smallest nitrogen mustard – namely HN2 – was considered. Indeed, as indicated by the results of the calculations on the isolated molecules (see Results and discussion and SI), the three azoyprites share remarkably similar properties. Such a similarity suggests that the adsorption behavior of HN2 may be considered as representative of this class of CWAs.

For the systems containing HN2 or DPGME adsorbed on regular and oxygen-enriched ZnO surfaces, the energetically preferred adsorption geometries were identified prior to the calculation of adsorption and electronic properties. To this end, several physically reasonable starting configurations were considered for each adsorbate–surface pair, including adsorption on Zn sites located both close to and farther from the oxygen adatoms in the oxygen-enriched models (see the SI, Section S3.2). The resulting optimized geometries of relevant alternative adsorption configurations are shown in Fig. S6, while their relative energies and selected interatomic distances are reported in Table S8. The minimum-energy adsorption structures were identified by energy comparison and subsequently used for the evaluation of adsorption energies (E_{ads}), interaction energies (E_{int}), deformation energies (E_{def}), and the electronic properties discussed in the main text.

The adsorption energies were computed using the expression:

$$E_{\text{ads}} = E_{\text{tot}} - (E_{\text{surf}} + E_{\text{mol}}) \quad (1)$$

where E_{tot} = total energy of the optimized surface with the adsorbed molecule; E_{surf} = energy of the optimized clean surface; and E_{mol} = energy of the optimized isolated molecule (calculated with the same approach used for all the periodic slab models). The interaction energies were computed using the same formal expression (eqn (1)), but in this case the energy terms E_{surf} and E_{mol} correspond to the single-point energies of the individual molecular (DPGME or HN2) and slab constituents, extracted from the minimum energy structure of the combined systems without performing further geometry optimization. Accordingly, deformation energies (E_{def}) for each system were estimated as $E_{\text{def}} = E_{\text{ads}} - E_{\text{int}}$.

In all the geometry optimizations of periodic models, ultra-soft pseudopotentials^{57,58} were used for Zn, Cl, O, N, C and H atoms, in conjunction with the PBE functional,⁵⁹ which provides a reliable description of oxide materials' structural

properties.^{60–68} Corrections to dispersion interactions were included by using the D3-bj empirical model,⁶⁹ which appreciably improves the description of systems where weak non-covalent interactions may play a significant role.⁷⁰ The valence electrons adopted for each species are: Zn $3d^{10}4s^2$; Cl $3s^23p^5$; O $2s^22p^4$; N $2s^22p^3$; C $2s^22p^2$ and H $1s^1$. Electronic states were expanded in plane waves up to a 25 Ry cutoff (240 Ry for the electron density).

On the optimized geometries, electronic structure analyses – density of states, work function, bader charge, charge density difference, electron localization functions, non covalent interaction calculations – were performed by adopting the DFT+*U* method, *i.e.*, by introducing the Hubbard *U* terms for Zn and O into the Hamiltonian.⁷¹ Indeed, according to previous theoretical studies on ZnO-based materials, the inclusion of the *U* term on both Zn and O atoms is necessary for an appropriate description of the p–d interaction.^{72,73} Specifically, the values selected for U_{Zn} and U_{O} are 12.0 eV and 6.5 eV, respectively, taken from the literature data.⁷⁴ Projector augmented-wave (PAW) pseudopotentials⁷⁵ were employed, up to a 35 Ry cutoff (240 Ry for the electron density). PAW pseudopotentials were taken from the Quantum ESPRESSO⁷⁶ library (<https://www.quantum-espresso.org/pseudopotentials/>). For each system, the electronic band gap value E_{G} was calculated as the difference between the conduction band (CB) and the valence band (VB) edges. The electronic structure type (p or n) of each model was determined from the computed density of states (DOS) by comparing the energies of the VB and CB edges with the Fermi level.^{77–80} All periodic calculations were performed by employing the Quantum ESPRESSO code.⁷⁶ Charge density difference analyses (CDD) were performed by subtracting from the electronic density of each surface-adsorbate system (ρ_{tot}) the electronic densities of the pertaining separated components (ρ_{surf} and ρ_{mol}), *i.e.*: $\Delta\rho = \rho_{\text{tot}} - \rho_{\text{surf}} - \rho_{\text{mol}}$. Electron localization functions (ELFs)⁸¹ were calculated with the post-processing tool included in the Quantum ESPRESSO distribution. In this case, norm-conserving pseudopotentials generated with the OPIUM code,⁸² taken from the Rappe Group repository (<https://www.sas.upenn.edu/rappegroup/research/pseudo-potential-gga.html>) were adopted for all atoms, with a wavefunction cutoff of 70 Ry (280 Ry for the density). Non-covalent-interaction (NCI) calculations⁸³ were performed with the CRITIC2 software.^{84,85} Bader charge analysis⁸⁶ was performed with the freely available Bader charge analysis code from the Henkelmann group.⁸⁷ For each system, the work function (Φ) was evaluated on the pertaining minimum energy structure, as the energy difference between the vacuum level and the Fermi energy of the system, using PAW pseudopotentials with a cutoff of 35 Ry. The vacuum level was obtained from the asymptotic value of the electrostatic potential in the vacuum region of the slab model. The electrostatic potential was extracted from self-consistent calculations and averaged over planes parallel to the surface, yielding a one-dimensional potential profile along the surface normal (*z* direction).^{16,88–90} This plane-averaged potential allows for a straightforward identification of the vacuum level from the plateau region sufficiently far from the slab. The work function

was then computed as the difference between this vacuum potential and the Fermi energy of the system.

Specifically, the vacuum level of the systems was calculated by applying the effective screening medium (ESM) method,⁹¹ which allows to eliminate spurious long-range electrostatic interactions due to periodic boundary conditions. This is achieved by immersing the slab between two semi-infinite vacuum regions.^{91,92} Further information on the computational details is reported in the SI.

Results and discussion

Molecular properties of isolated nitrogen mustard agents and their simulant

The azoyprites. Geometry optimizations of the three azoyprites $\text{C}_6\text{H}_{13}\text{Cl}_2\text{N}$ (HN1), $\text{C}_5\text{H}_{11}\text{Cl}_2\text{N}$ (HN2) and $\text{C}_6\text{H}_{12}\text{Cl}_3\text{N}$ (HN3) were performed using a DFT approach and subsequently refined at the MP2 level of theory. The resulting minimum energy structures are depicted in Fig. 2, while the key bond lengths and angles are summarized in Tables S2–S4 for HN1, HN2 and HN3, respectively (see the SI). A conformational search was also performed for each compound in order to identify possible alternative low-energy structures. The most energetically favorable conformers are shown in Fig. 2. As evidenced by the data reported in Tables S2–S4, the ωB97XD -geometrical parameters calculated for the minimum energy structures show a good agreement with those obtained at the MP2 level and with the available literature data.⁹³ Overall, the performance of this range-separated DFT functional to describe subtle molecular structure details, also highlighted in previous studies,⁹⁴ could be considered satisfactory, in view of its significantly lower computational cost *vs.* more accurate post-HF approaches.

To complement the geometrical analysis and gain further insight into the electronic properties of the azoyprites, molecular

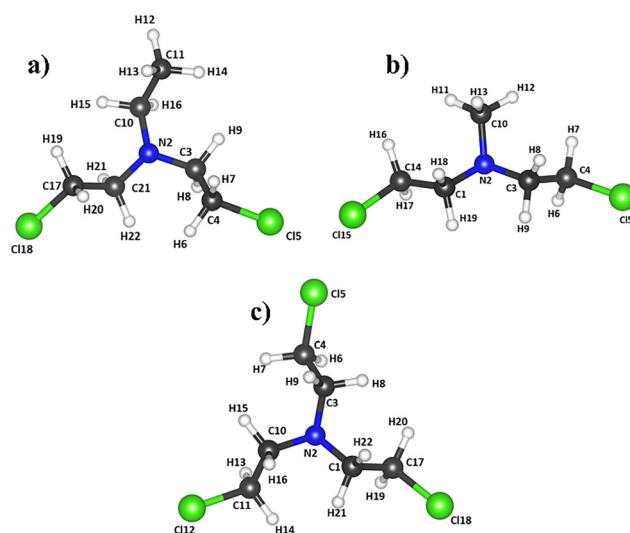


Fig. 2 Optimized molecular structures of (a) $\text{C}_6\text{H}_{13}\text{Cl}_2\text{N}$ (HN1), (b) $\text{C}_5\text{H}_{11}\text{Cl}_2\text{N}$ (HN2) and (c) $\text{C}_6\text{H}_{12}\text{Cl}_3\text{N}$ (HN3). Atom color code: Cl = green; N = blue; C = grey; H = white.

electrostatic potential (MEP) maps were computed at the DFT level for the optimized geometries of HN1, HN2, and HN3 (Fig. 3). These maps display a representation of the electron density distribution across the molecular surface and help to identify regions of potential intermolecular interactions. For the three nitrogen mustards, significant regions of negative electrostatic potential are localized around the central nitrogen atom and the chlorine atoms, highlighting electron-rich regions that may act as favorable sites for electrophilic interactions. Conversely, the carbon and hydrogen atoms are surrounded by areas of positive or mildly positive potential, suggesting electron-poor regions that may interact preferentially with nucleophiles. Concerning the negative potential regions, only the ones localized on chlorine atoms are easily accessible, while the nitrogen atom is screened by the positive methyl- and methylene group regions (see Fig. 3).

The molecular geometry of DPGME was optimized in a vacuum at the ω B97XD/6-311+G(d,p) level, leading to a linear structure, displayed in SI, Fig. S1. Particular attention was then paid to the potential formation of an intramolecular hydrogen bond between the hydroxyl group and an ether oxygen atom. To explore this hypothesis, a conformational search was carried out to identify alternative low-energy structures potentially stabilized by such an interaction. Among the generated conformers, a folded isomer, previously unreported in the literature, was found to exhibit a strong intramolecular H-bond, as illustrated in Fig. 4.

Notably, this folded conformer was calculated to be $4.15 \text{ kcal mol}^{-1}$ more stable than the linear structure (including zero-point energy), and it is therefore expected to be the preferred isomer under gas phase conditions. Both conformers were further optimized at the MP2/6-311+G(d,p) level. Even the MP2 results identified the folded conformer as the most stable structure, with an energy difference of $3.75 \text{ kcal mol}^{-1}$ relative to the linear geometry. Selected bond lengths and angles are reported in Table S5, as obtained from both DFT and MP2 calculations. A comparison of the geometrical parameters at the ω B97XD and MP2 levels of theory reveals only minor variations in both bond lengths and angles.

Following the same procedure adopted for the three azopyrites, the molecular electrostatic potential was calculated for the most stable DPGME conformer, namely the folded isomer. As shown in Fig. 5, the red-colored regions surrounding the oxygen atoms (both hydroxyl and ether) correspond to areas of

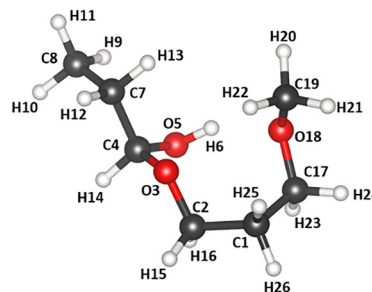


Fig. 4 Optimized molecular structure of DPGME in its folded conformation. The structure is stabilized by an intramolecular hydrogen bond ($\text{O5} \cdots \text{H6}$, $d = 1.881 \text{ \AA}$ at the MP2/6-311+G(d,p) level). Atoms color code: C = grey; O = red; H = white.

negative electrostatic potential, indicating negative potential and thus nucleophilic character. Conversely, the green/blue regions, located around the methyl and methylene groups, indicate positive potential, thus making them prone to nucleophilic attack.

In addition, the HOMO–LUMO energy gap ($\Delta E_{\text{H-L}}$) was computed for each species and is reported in Table S6. Remarkably, the calculated $\Delta E_{\text{H-L}}$ values for the three nitrogen mustards are comparable to that of DPGME. This result is of particular relevance, given that the chemical reactivity of molecular systems could be, in general, influenced by the frontier orbitals and their energy difference.⁹⁵

Adsorption on stoichiometric and O-enriched $\text{ZnO}(10\bar{1}0)$

Geometry optimization calculations of the adsorption of HN2 and DPGME on stoichiometric $\text{ZnO}(10\bar{1}0)$ slab models indicated that both molecules are stably physisorbed on the regular $\text{ZnO}(10\bar{1}0)$ surface (Fig. 6).

The adsorption of the vesicant HN2 involves its two terminal chlorine atoms coordinating to two top-layer Zn cations (Fig. 6a). This interaction is associated with Zn–Cl bond lengths of $2.52 \text{ \AA}$, and an adsorption energy of $-30.69 \text{ kcal mol}^{-1}$ (Table 1). Also, a methylene proton interacts with a surface oxygen atom at a distance of $2.17 \text{ \AA}$. The HN2 C–Cl bonds involved in the interaction with the surface undergo a modest lengthening (from 1.80 to $1.82 \text{ \AA}$) with respect to the values pertaining to the isolated molecule, calculated with the same approach. Similarly, the DPGME molecule (Fig. 6b) is oriented

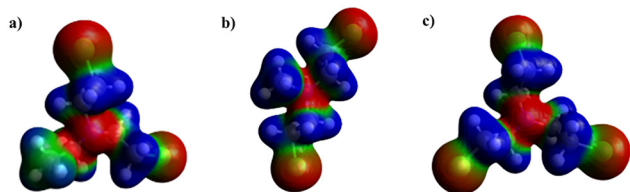


Fig. 3 Molecular electrostatic potential (MEP) map of (a) HN1, (b) HN2 and (c) HN3 projected onto the electron density isosurface. Red regions correspond to areas of negative electrostatic potential, while green/blue regions indicate positive electrostatic potential.

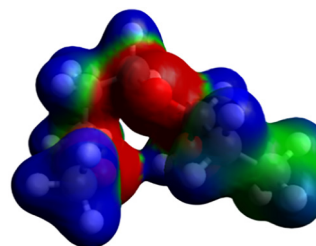


Fig. 5 MEP map of the most stable DPGME conformer (Fig. 4). The MEP is projected onto the electron density isosurface: red regions correspond to areas of negative electrostatic potential, while green and blue regions indicate positive electrostatic potential.

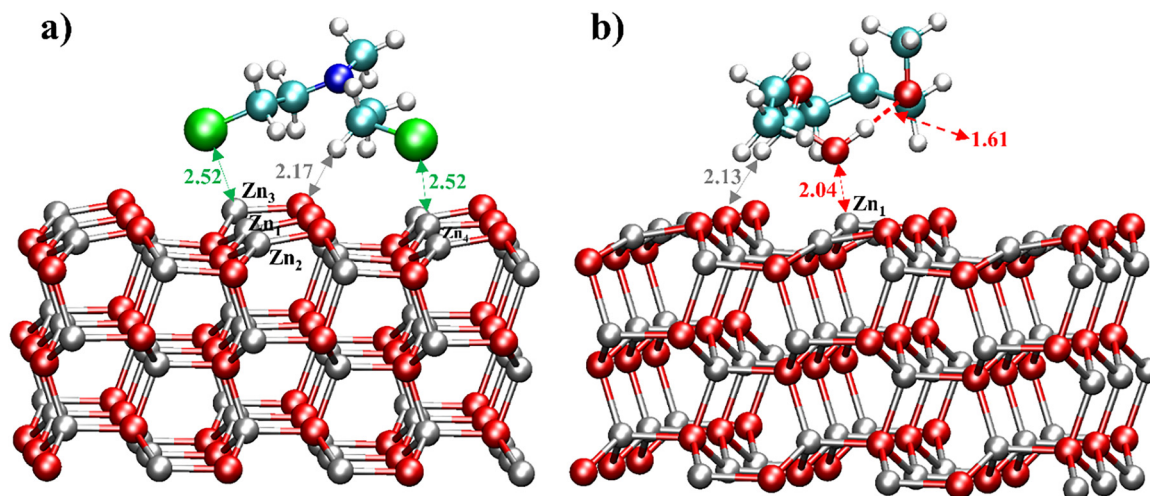


Fig. 6 Minimum energy structures of (a) HN2 and (b) DPGME on the regular ZnO(10 $\bar{1}$ 0) surface. Double-arrow lines indicate relevant interatomic separations (values in Å). The intramolecular hydrogen bond in DPGME is shown as a red dashed line. Atom color code: Zn = grey; O = red; Cl = light green; N = blue; C = cyan; H = white.

with the two terminal methyl groups pointing towards the surface, with a methylene proton at a close distance (2.13 Å) from a top-layer oxygen. The hydroxyl oxygen involved in the intramolecular hydrogen bond interacts with a surface Zn site (Zn₁), forming a coordination bond characterized by a distance of 2.04 Å. Interestingly, the intramolecular hydrogen bond in DPGME becomes stronger upon coordination to the surface, with the hydrogen bond distance changing from 1.86 Å to 1.61 Å. The DPGME adsorption energy is $-33.42 \text{ kcal mol}^{-1}$ (Table 1), *i.e.*, slightly greater than HN2. The preferential interaction sites of both molecules are consistent with the MEP maps, which indicated high negative electrostatic potential on the chlorine atom regions of HN2 (Fig. 3) and on the hydroxyl oxygen region of DPGME (Fig. 5).

Based on these findings, several similarities emerge between HN2 and its simulant DPGME. In both cases, adsorption occurs through coordination of electron-rich molecular regions to exposed surface Zn cations, resulting in comparable adsorption geometries despite the different nature of the donor atoms involved. Importantly, the adsorption energies are also very similar, differing by only $2.73 \text{ kcal mol}^{-1}$ (Table 1). Likewise, the interaction energies E_{int} differ by only $2.86 \text{ kcal mol}^{-1}$, indicating comparable intrinsic molecule–surface interaction strengths. These observations suggest that HN2 and DPGME exhibit similar affinities towards the stoichiometric ZnO(10 $\bar{1}$ 0) surface, supporting the suitability of DPGME as a simulant for nitrogen mustard adsorption studies.

The adsorption energetics obtained in the present work are also consistent with previous computational investigations of chemical warfare agents and related simulants on ZnO surfaces. In particular, adsorption energies reported for sarin³⁸ and DMMP⁴¹ on ZnO(10 $\bar{1}$ 0) (-31.9^{38} and $-33.9^{41} \text{ kcal mol}^{-1}$, respectively) are remarkably similar to those obtained here for HN2 and DPGME. In all cases, adsorption involves coordination of electron-rich molecular sites to exposed Zn centres, yielding characteristic adsorbate–surface distances in the 2.0–2.5 Å range (see Table S7 in the SI). Similar adsorption motifs have also been reported for DMMP adsorption on a ZnO nanosheet.⁴³ In a broader perspective, by considering other metal oxides, comparable adsorption geometries have been reported for DMMP adsorption on TiO₂,⁴⁰ MoO₃,⁴² and Al₂O₃³⁷ surfaces, although somewhat stronger adsorption energies were found for these materials. Overall, these comparisons provide additional support for the physical plausibility and consistency of the adsorption structures and energetics obtained in the present work.

Since the addition of either atomic or molecular oxygen to metal oxide semiconductor (MOX) surfaces has been experimentally shown to enhance the detection of CWAs,^{17,21} the interaction of HN2 and DPGME with oxygen-enriched ZnO surfaces was also investigated. This choice is based on the widely accepted sensing mechanism of MOX-based chemiresistive devices.^{12,21} Under operating conditions typically ranging from 150 to 400 °C, the ZnO surface can host a variety of oxygen species.^{12,13} Such adsorbed species are hypothesized to act as

Table 1 Adsorption energies (E_{ads}), adsorption energy differences ($\Delta E_{\text{ads}} = E_{\text{ads}}(\text{HN2}) - E_{\text{ads}}(\text{DPGME})$), interaction energies (E_{int}), interaction energy differences ($\Delta E_{\text{int}} = E_{\text{int}}(\text{HN2}) - E_{\text{int}}(\text{DPGME})$), deformation energies ($E_{\text{def}} = E_{\text{ads}} - E_{\text{int}}$), and deformation energy differences ($-\Delta E_{\text{def}} = E_{\text{def}}(\text{HN2}) - E_{\text{def}}(\text{DPGME})$) for DPGME and HN2 adsorbed on regular and oxygen-enriched ZnO(10 $\bar{1}$ 0) surfaces. All energies in kcal mol^{-1}

Surface	$E_{\text{ads}}(\text{HN2})$	$E_{\text{ads}}(\text{DPGME})$	ΔE_{ads}	$E_{\text{int}}(\text{HN2})$	$E_{\text{int}}(\text{DPGME})$	ΔE_{int}	$E_{\text{def}}(\text{HN2})$	$E_{\text{def}}(\text{DPGME})$	$-\Delta E_{\text{def}}$
ZnO	−30.69	−33.42	2.73	−36.23	−39.09	2.86	5.54	5.67	0.06
ZnO + O	−31.06	−32.99	1.93	−36.91	−42.68	5.77	5.85	9.69	3.84
ZnO +2O	−32.40	−32.48	0.08	−37.22	−42.03	4.81	4.82	9.55	4.73

electron acceptors, creating surface depletion layers that modulate the semiconductor's response upon exposure to reducing gases. The ability of MOX surfaces to incorporate such oxygen species is therefore considered a key feature for selective analyte recognition.^{12,17} To simulate these conditions, one should perform finite temperature simulations, *e.g.* *ab initio* molecular dynamics approaches. Here we focus on the 0 K analysis, namely, we perform the study solely on optimized geometries to identify similarities and differences in the adsorption motifs of HN2 and DPGME on O-rich ZnO surfaces.

To this aim, two oxygen-enriched ZnO(10 $\bar{1}$ 0) slab models were constructed: one incorporating a single oxygen adatom (Fig. 1b), and one including a chemisorbed O₂ molecule (Fig. 1c). In both optimized structures, the oxygen adatoms – denoted as O1 and O2 – are bound to surface oxygen atoms (O_{s1} and O_{s2}, respectively), with O–O distances of 1.527 Å, thus forming peroxo-like surface species. In the ZnO + O model (Fig. 1b), O1 lies 2.007 Å from the nearest Zn atom (Zn₁), with an O_{s1}–O1–Zn₁ angle of 102.3°. In the ZnO + 2O system (Fig. 1c), the corresponding O–Zn distances are 2.027 Å, while the O_s–O–Zn angles are both 103.5°.

The O1–O2 distance is 3.413 Å. These model surfaces could enable the assessment of how an increasing oxygen coverage affects the adsorption behavior of HN2 and DPGME, and the role of O-enriched ZnO surfaces in sensing applications.

The optimized adsorption structures of HN2 and DPGME on ZnO + O and ZnO + 2O are shown in Fig. 7. Overall, the peroxo-like arrangement of oxygen adatoms remains largely unaffected by adsorption of either HN2 or DPGME (Fig. 7a–d), suggesting weak interaction between the adsorbates and these surface defects. Although HN2 is coordinated to a Zn site (Zn₁) close to the oxygen adatom O1 (Fig. 7a and c), the Cl–O1 distances are 3.67 Å and 3.68 Å on ZnO + O and ZnO + 2O, respectively, corroborating the hypothesis of a weak adsorbate–defect interaction. Even more remarkably, on both oxygen-enriched surfaces, DPGME preferentially coordinates to a Zn site (Zn₄) distant from the oxygen adatoms (Fig. 7b and d), further supporting the view that direct interactions between the adsorbates and the peroxo-type defects are weak. Notably, the intramolecular hydrogen bond in DPGME becomes shorter, indicating a strengthening of this interaction with increasing oxygen coverage. Nonetheless, key

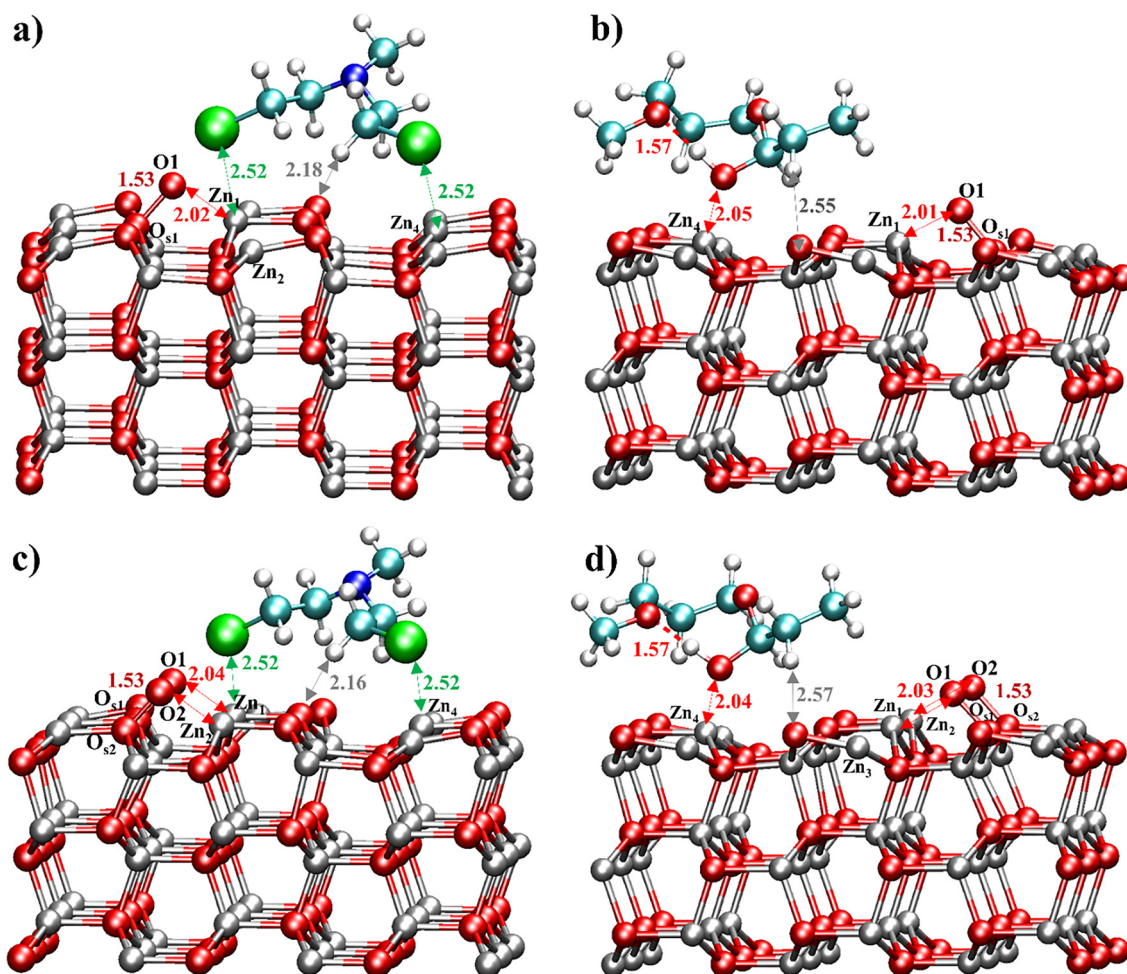


Fig. 7 Minimum energy structures of (a) HN2 on ZnO + O, (b) DPGME on ZnO + O, (c) HN2 on ZnO + 2O, and (d) DPGME on ZnO + 2O. Double-arrow lines indicate relevant interatomic separations (values in Å). The intramolecular hydrogen bond in DPGME is shown as a red dashed line. Atom color code: Zn = grey; O = red; Cl = light green; N = blue; C = cyan; H = white.

interaction distances remain essentially unchanged with respect to those obtained for stoichiometric ZnO(10 $\bar{1}$ 0). For HN2, the Zn–Cl distances are 2.52 Å on both mono- and di-oxygenated surfaces, matching those of the regular surface. Similarly, for DPGME, the Zn–O coordination distance is comparable to that found on stoichiometric ZnO.

To further assess the robustness of the proposed adsorption modes, additional adsorption configurations were optimized for both HN2 and DPGME on the stoichiometric and oxygen-enriched ZnO(10 $\bar{1}$ 0) surfaces. In all cases, the minimum energy adsorption geometries discussed in the main text were found to be energetically preferred, while alternative adsorption arrangements were higher in energy by 4–13 kcal mol^{−1} (see Fig. S6 and Table S8 in the SI). In particular, for the oxygen-enriched surfaces, adsorption of DPGME on Zn sites located adjacent to the oxygen adatoms was found to be energetically disfavoured, supporting the adsorption geometries reported in Fig. 7.

For the minimum energy structures, the corresponding adsorption energies are reported in Table 1. Importantly, despite the different preferred adsorption arrangements identified for HN2 and DPGME on the oxygen-enriched surfaces, the differences in adsorption energy remain very small across all surface models, with ΔE_{ads} values of 1.93 kcal mol^{−1} for ZnO + O, and 0.08 kcal mol^{−1} for ZnO + 2O.

A more direct estimate of the intrinsic strength of surface-molecule interactions can be obtained from the data in Table 1. The interaction-energy analysis reveals that DPGME establishes stronger molecule–surface interactions than HN2 on oxygen-enriched ZnO surfaces. However, this enhanced stabilization is accompanied by a significantly larger deformation energy E_{def} . Actually, the energetic cost of the deformation is particularly severe for DPGME with respect to HN2 on the di-oxygenated surface ($\Delta E_{\text{def}} = 4.73$ kcal mol^{−1}). As a result, the final adsorption energies remain remarkably similar for the two molecules. These findings indicate that the comparable adsorption behaviour of HN2 and DPGME arises from a balance between interaction and deformation contributions rather than from identical molecule–surface interaction strengths.

Overall, HN2 and DPGME are expected to produce similar responses on ZnO surfaces, with the agreement becoming even closer as oxygen coverage increases. Indeed, these analyses indicate that DPGME could act as an effective simulant for ZnO-based sensors with significant oxygen adatom coverage. Further insight into this aspect can be gained by analysing the electronic properties of the systems.

Electronic structure modulation upon adsorption of DPGME and HN2 on ZnO(10 $\bar{1}$ 0)

A thorough insight into the electronic structure changes induced by the adsorption of DPGME and HN2 on ZnO(10 $\bar{1}$ 0) surfaces can be obtained through Bader charge analysis,⁹⁶ charge density difference (CDD), electron localization function (ELF), non-covalent interaction (NCI) analyses, and density of states (DOS) calculations. These real-space electronic descriptors have previously been employed to investigate the interaction of nitrogen mustard agents with a variety of materials,

Table 2 Bader charge values (in units of *e*) for HN2 and DPGME physisorbed on regular and O-enriched ZnO(10 $\bar{1}$ 0) surfaces

System	ZnO	ZnO + O	ZnO + 2O
HN2	0.174	0.176	0.149
DPGME	0.092	0.095	0.093

including low-dimensional nanostructures^{97–99} and supramolecular hosts.¹⁰⁰ In the present work, they are applied to the adsorption of HN2 and DPGME on ZnO surfaces to provide a more detailed characterization of the adsorbate–surface interaction and the associated electronic redistribution.

Firstly, the Bader charge values (Table 2) indicate that both molecules act as electron donors toward both regular and oxygen-enriched ZnO(10 $\bar{1}$ 0) surfaces, as already suggested by the electrostatic potential maps of the isolated species (Fig. 3 and 5). In particular, for HN2 the charge transfer to stoichiometric ZnO amounts to 0.174*e*, with a very similar value obtained for ZnO + O (0.176*e*) and a slight decrease for ZnO + 2O (0.149*e*). Interestingly, in all cases DPGME donates a smaller amount of charge (0.092–0.095*e*), indicating a weaker electronic interaction with ZnO compared to HN2.

An intuitive understanding of the electronic interactions between the adsorbates (HN2 and DPGME) and the surfaces can be obtained through CDD analysis. CDD maps were calculated to visualize the electronic redistribution induced by adsorption on regular and oxygen enriched ZnO(10 $\bar{1}$ 0) surfaces (Fig. 8). For both HN2 and DPGME, electron depletion (green regions) is mainly observed in the molecular regions directly involved in surface coordination, *i.e.* around the oxygen and chlorine atoms, respectively. Such a depletion is accompanied by electron accumulation (yellow regions) on the coordinating Zn sites, as well as on the neighbouring surface oxygen atoms. These results are consistent with the Bader charge analysis, which indicates net charge transfer from the adsorbates to the oxide. Moreover, the charge redistribution remains largely localized around the adsorption site, suggesting that adsorption is mainly governed by localized donor–acceptor interactions rather than by extensive covalent bond formation.

To further characterize the nature of the adsorption process, NCI analyses were performed for all investigated systems (Fig. 9). Such an approach allows one to identify the main noncovalent interactions responsible for surface adsorption, and to establish whether they are localized to a few atoms or are evenly distributed over the molecule–surface contact region. In the case of HN2, localized attractive interaction regions are found between both chlorine atoms and the coordinated Zn surface sites, in agreement with the adsorption geometries obtained from structural optimization and with the CDD plots. For DPGME, the attractive region is mainly associated with the binding between the hydroxyl oxygen atom and the Zn site, while a more spatially distributed pattern of weak interactions is also observed around the adsorption region. Overall, the NCI analysis confirms that adsorption is dominated by noncovalent attractive interactions localized around the key molecule–surface contacts.

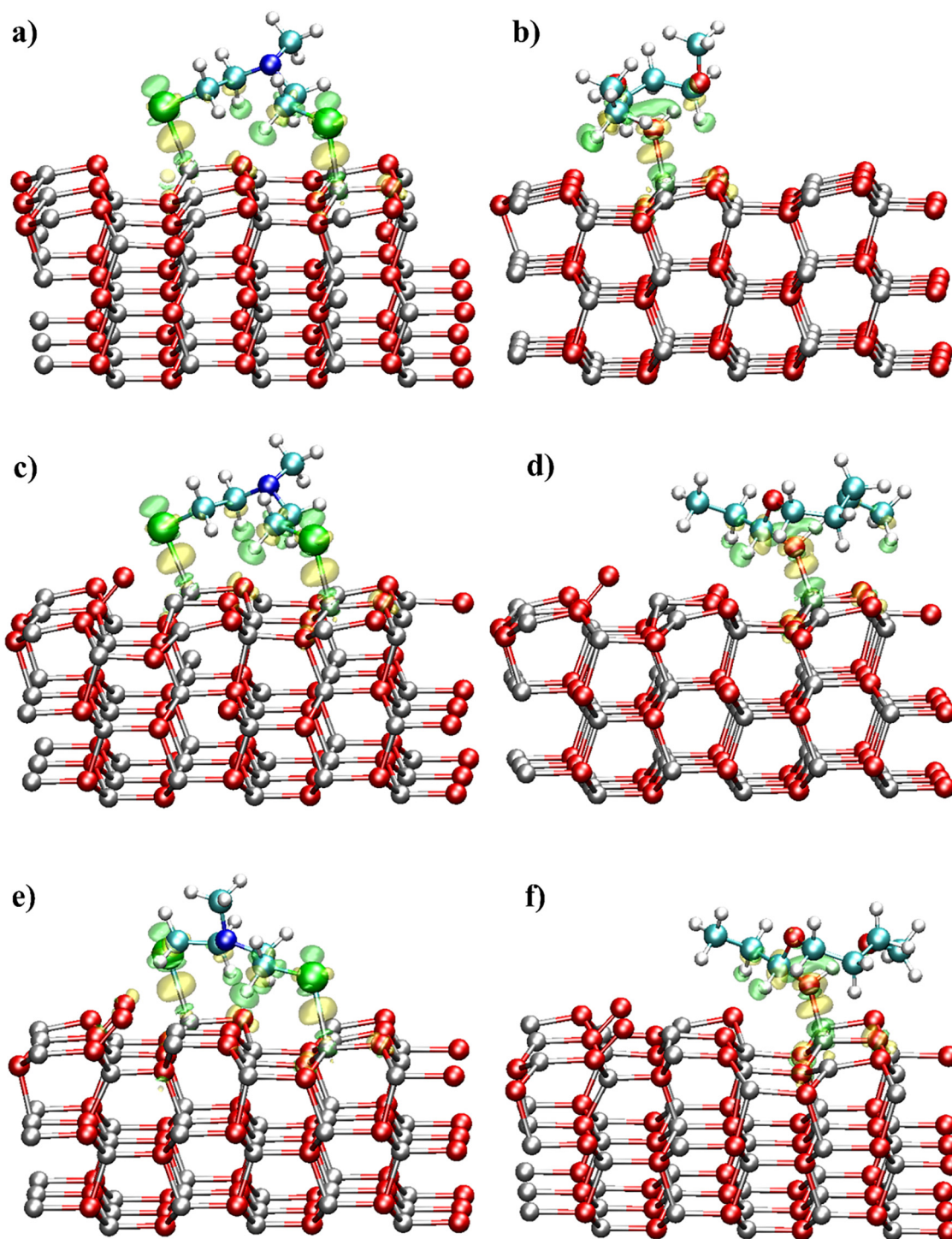


Fig. 8 Charge density difference (CDD) maps for the systems: (a) ZnO + HN2; (b) ZnO + DPGME; (c) ZnO + O + HN2; (d) ZnO + O + DPGME; (e) ZnO + 2O + HN2; and (f) ZnO + 2O + DPGME. All CDDs were computed using an isosurface level of $0.03 \text{ \AA}^{-3}$. Regions of electron accumulation are shown in yellow, whereas regions of electron depletion are shown in light green. Atoms color code as in Fig. 7.

Additional insight into the interaction of HN2 and DPGME with stoichiometric and oxygen-enriched ZnO can be gathered by plotting the ELF along the Zn–Cl and Zn–O directions, respectively. In general, whereas $\text{ELF} = 1$ indicates complete electron localization, $\text{ELF} = 0$ represents full delocalization. Accordingly, high ELF values are typically associated with the presence of lone

pairs or covalent bonds.⁸¹ In the present case, the ELF maps shown in Fig. 10 reveal that the regions of high electron localization remain primarily associated with the adsorbate donor atoms and the surface atoms, while no pronounced ELF maxima are observed in the intermolecular region between the adsorbate and Zn sites. This result indicates that, for both the mustard agent and

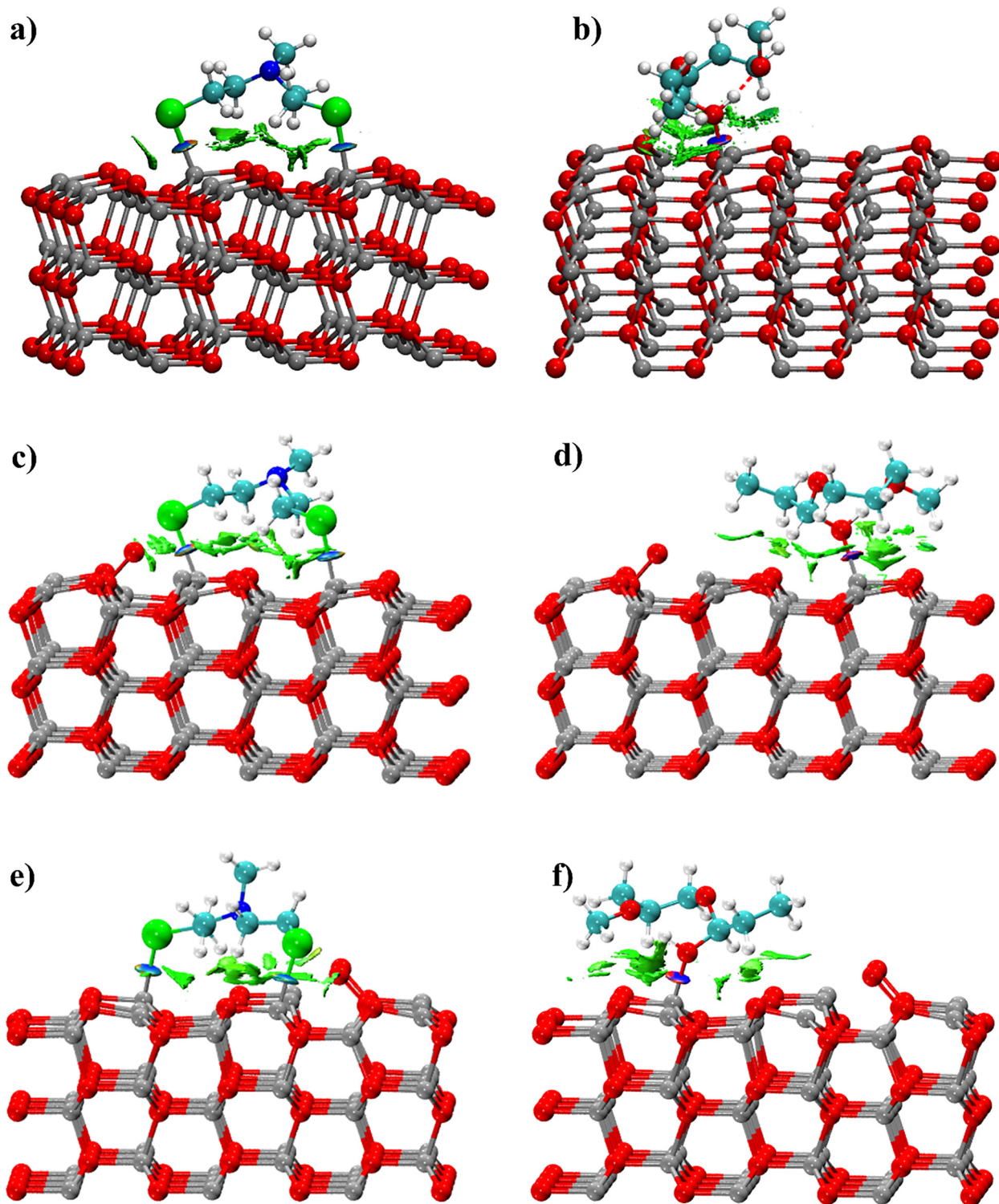


Fig. 9 NCI plots for the systems: (a) ZnO + HN₂; (b) ZnO + DPGME; (c) ZnO + O + HN₂; (d) ZnO + O + DPGME; (e) ZnO + 2O + HN₂; and (f) ZnO + 2O + DPGME (isovalue of 0.5 a.u.). Green shaded areas represent regions dominated by dispersion interactions, while blue disk-shaped regions indicate strong donor–acceptor interactions.

its simulant, adsorption on either stoichiometric or oxygen-enriched surfaces does not involve the formation of strongly covalent bonds and is consistent with a predominantly closed-shell donor–acceptor interaction picture.

Further insight is provided by DOS analysis, whose results are summarized in Table 3 (see also SI, Fig. S7–S9 for DOS plots). Interestingly, while stoichiometric ZnO(10 $\bar{1}$ 0) exhibits an n-type character, the presence of oxygen adatoms induces a change to

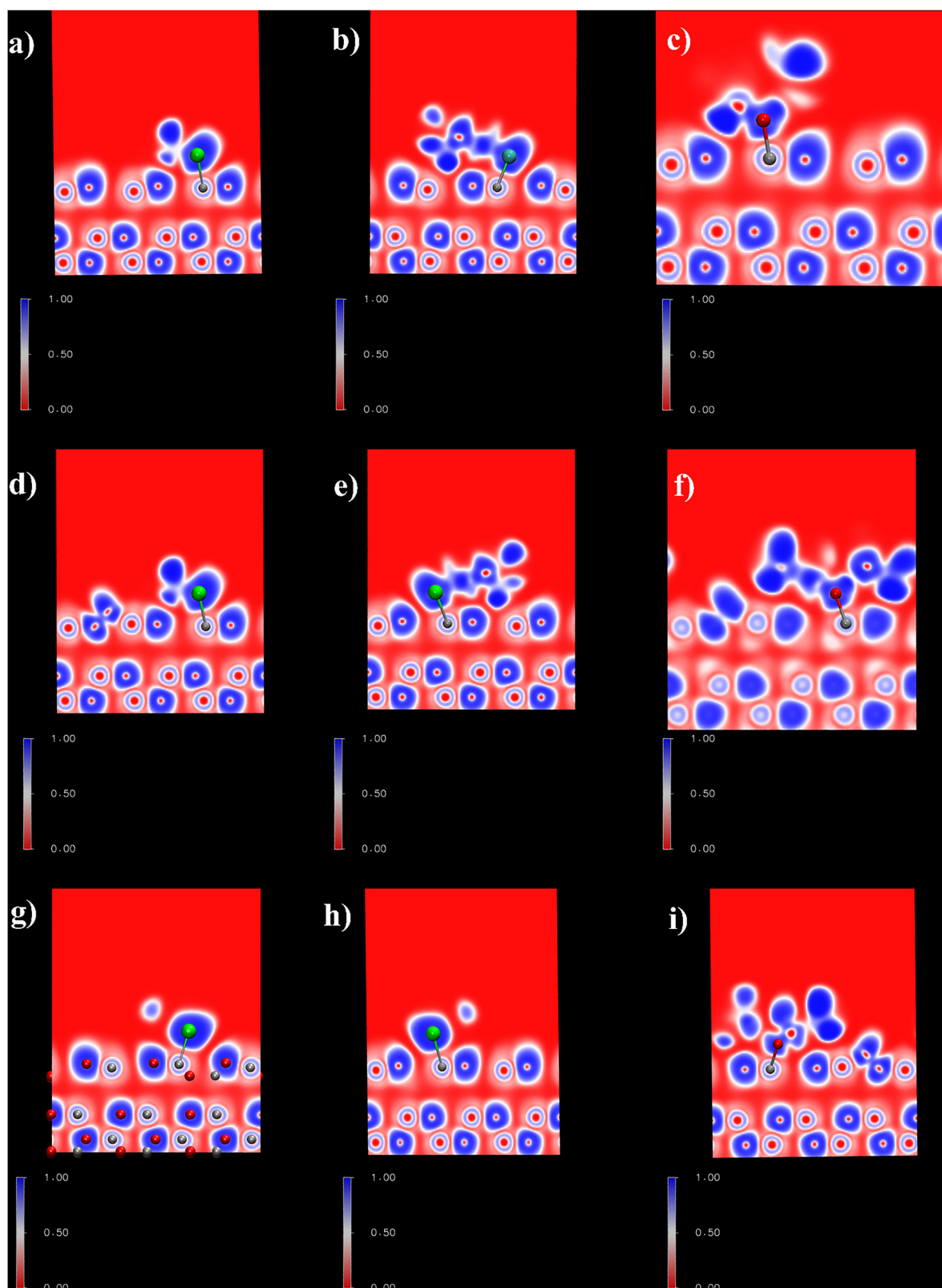


Fig. 10 Electron localization function (ELF) contour plots computed along the surface-adsorbate coordination: (a) Zn–Cl1 (ZnO + HN2); (b) Zn–Cl2 (ZnO + HN2); (c) Zn–O (ZnO + DPGME); (d) Zn–Cl1 (ZnO + O + HN2); (e) Zn–Cl2 (ZnO + O + HN2); (f) Zn–O (ZnO + O + DPGME); (g) Zn–Cl1 (ZnO + 2O + HN2); (h) Zn–Cl2 (ZnO + 2O + HN2); and (i) Zn–O (ZnO + 2O + DPGME). Blue and red colors represent high- and low-electron-localization regions, respectively.

Table 3 Band gap energy (E_G , in eV), and work function changes with respect to stoichiometric ZnO(10 $\bar{1}$ 0) ($\Delta\Phi$, in eV) calculated for regular and O-enriched ZnO(10 $\bar{1}$ 0) slab models, and upon adsorption of HN2 and DPGME. For comparison, the calculated E_G for bulk ZnO amounts to 2.70 eV

System	E_G (eV)	Type	$\Delta\Phi$
ZnO	2.28	n	0
ZnO + HN2	2.17	n	−1.40
ZnO + DPGME	2.29	n	−1.44
ZnO + O	2.10	p	0.59
ZnO + O + HN2	2.18	n	−1.06
ZnO + O + DPGME	2.19	n	−1.24
ZnO + 2O	1.86	p	0.72
ZnO + 2O + HN2	1.92	n	−0.91
ZnO + 2O + DPGME	1.89	n	−1.23

p-type behaviour, which becomes more pronounced with increasing oxygen coverage. This trend is consistent with experimental evidence showing that oxygen-rich ZnO samples typically exhibit a p-type character.^{28,31,33}

In addition, the calculated band gap decreases from 2.28 eV for stoichiometric ZnO to 2.10 eV (ZnO + O) and 1.86 eV (ZnO + 2O), indicating that oxygen adatoms significantly affect the electronic structure of the material.

Upon adsorption of HN2 and DPGME, the DOS of stoichiometric ZnO is only weakly perturbed. In contrast, for oxygen-enriched surfaces, adsorption induces a marked shift of the Fermi level towards the conduction band, resulting in a transition from p-type to n-type character. Conductivity-type switching phenomena of this kind have attracted considerable attention in the gas-sensing literature, as they cannot be readily explained by conventional sensing models based solely on carrier-concentration modulation within a semiconductor of fixed conductivity type.^{28–31} In this context, the present results suggest that oxygen-related surface species may contribute to p–n/n–p switching behaviour through adsorption-induced charge transfer and electronic structure modifications. Therefore, the calculations provide atomistic insight into a phenomenon of growing interest in ZnO-based chemiresistive sensing materials.

Importantly, HN2 and DPGME induce closely comparable changes in both charge transfer and electronic structure across all surface models. In particular, both molecules preserve the n-type character of stoichiometric ZnO and induce analogous p-to-n switch on oxygen-enriched surfaces. These findings further support the suitability of DPGME as a simulant for nitrogen mustard agents in ZnO-based sensing applications.

Additional insight is provided by projected DOS (pDOS) analysis (Fig. 11 and Fig. S10, SI). In all systems, the valence band edge is dominated by O 2p states, including contributions from peroxy species when present, while the conduction band minimum is mainly composed of Zn 4s and 4p states (Fig. S10, SI). This electronic structure remains largely unchanged upon adsorption. The pDOS pertaining to both HN2 and DPGME (Fig. 11) are mainly located in the vicinity of the valence-band edge, with negligible contributions to the conduction band. This finding indicates that adsorption does not introduce significant adsorbate-derived states near the conduction-band edge. The similar overall distribution of

the adsorbate-derived states further supports the comparable electronic response induced by HN2 and DPGME upon adsorption on ZnO surfaces. Notably, the highest-energy valence states associated with DPGME (mainly O(2p) and C(2p)) are located closer to the valence-band edge, whereas the corresponding HN2-derived states are shifted to lower energies by approximately 0.5 eV. This difference reflects the distinct electronic structures of the two adsorbates, although the overall electronic perturbation induced on the ZnO surface remains qualitatively similar.

To further elucidate the electronic structure changes induced by oxygen species and by the adsorption of HN2 and DPGME on ZnO(10 $\bar{1}$ 0), the variation of the work function ($\Delta\Phi$) with respect to the stoichiometric surface was evaluated.

Bader charge analysis (Table 2) indicated that the presence of oxygen adatoms and/or adsorbates induces charge redistribution at the interface. Consistently, DOS calculations revealed significant modifications of the electronic structure upon both oxygen enrichment and molecular adsorption.

The work function reflects the energy required to remove an electron from the system and is therefore sensitive to charge redistribution. In particular, electron donation from the adsorbate to the surface is expected to decrease the work function, whereas electron withdrawal leads to the opposite effect.

In the present case, both HN2 and DPGME act as electron donors, as confirmed by Bader analysis. Accordingly, their adsorption on ZnO(10 $\bar{1}$ 0) results in a marked decrease of the work function for all surface models (Table 3). Notably, $\Delta\Phi$ values are consistently negative, irrespective of the presence of oxygen adatoms, indicating a similar electronic response of the substrate to both molecules.

Conversely, oxygen enrichment of the surface leads to a significant increase in the work function, with $\Delta\Phi$ values of +0.59 and +0.72 eV for the mono- and di-oxygenated models, respectively. This behaviour is consistent with the electron-withdrawing character of oxygen species and with the corresponding modification of the surface electronic structure, in agreement with experimental observations on ZnO-based sensors.^{28–31}

Interestingly, although HN2 exhibits a larger charge transfer to the surface than DPGME, the latter induces a slightly more pronounced decrease in the work function. This observation indicates that work-function variations cannot be rationalized solely in terms of the amount of transferred charge. A possible qualitative rationale may reside in the different adsorption geometries of the two molecules: DPGME interacts with the surface through a single, relatively short Zn–O coordination bond, whereas HN2 adsorption involves two longer Zn–Cl interactions. Such differences may influence the spatial pattern of the adsorption-induced electronic density redistribution at the interface, which is known to affect work-function variations.^{16,88–90}

Conclusions

In this work, the adsorption behaviour of nitrogen mustard (HN2) and its simulant (DPGME) on stoichiometric and oxygen-

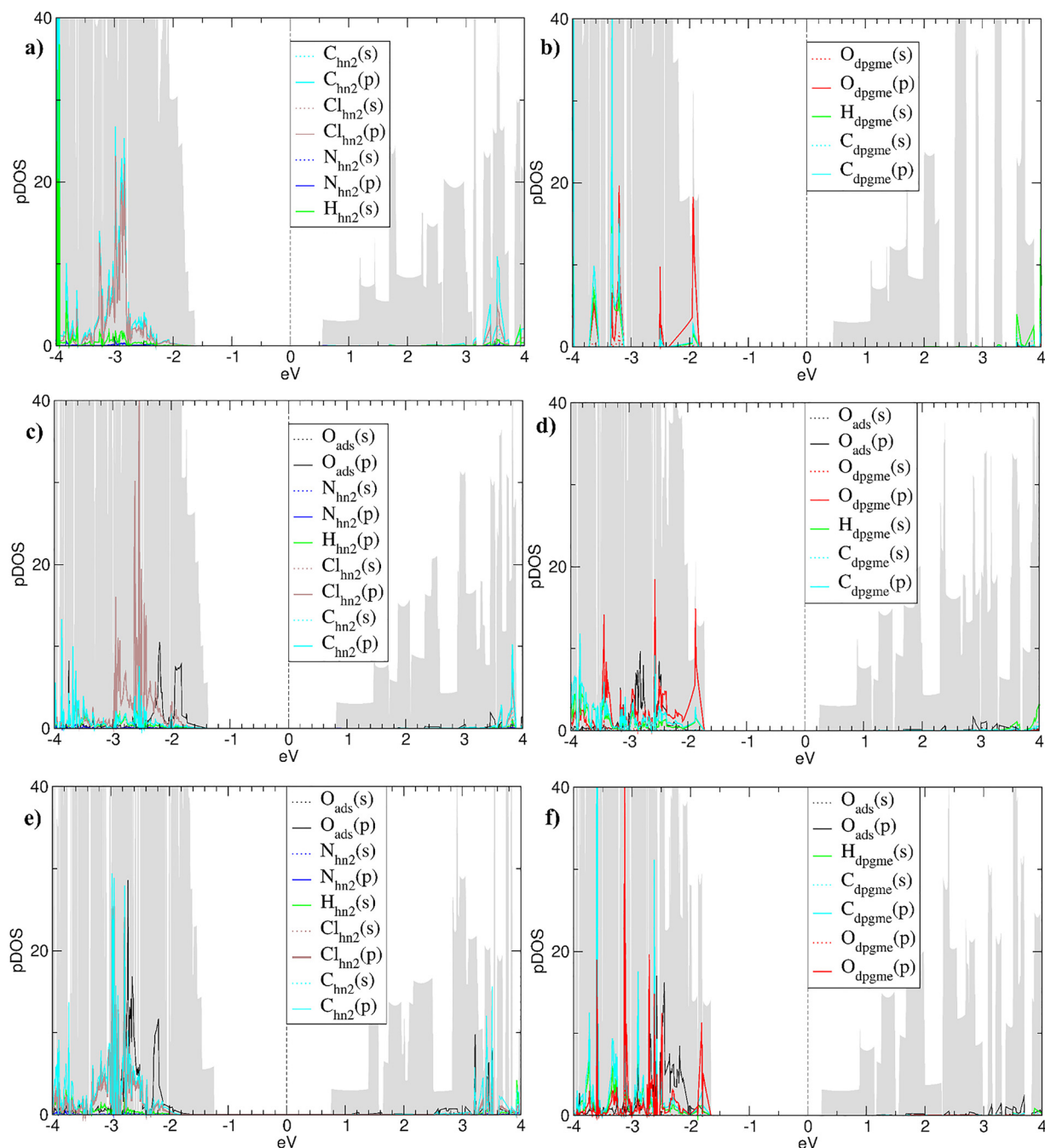


Fig. 11 Projected density of states (pDOS) of the adsorbates' atoms for the systems: (a) ZnO + HN₂; (b) ZnO + DPGME; (c) ZnO + O + HN₂; (d) ZnO + O + DPGME; (e) ZnO + 2O + HN₂; and (f) ZnO + 2O + DPGME. The vertical dashed line represents the position of the Fermi level, conventionally set to 0. The grey-shaded area represents the total DOS. For improved readability, enlarged versions of the pDOS plots are provided in Fig. S11–S13 of the SI.

enriched ZnO(10 $\bar{1}$ 0) surfaces has been investigated using density functional theory-based methods.

Both molecules interact with the surface through coordination to exposed Zn sites, exhibiting comparable adsorption energies across all surface models, with the closest agreement observed at higher oxygen adatom coverage. In all cases, electron transfer from the adsorbates to the oxide is predicted.

The combined structural, energetic, and electronic analyses consistently indicate that DPGME reproduces the adsorption

behaviour of HN₂ on ZnO(10 $\bar{1}$ 0) surfaces despite the substantial structural differences between the two molecules. Comparable interaction energies, charge-transfer characteristics, and adsorption-induced electronic responses support the suitability of DPGME as a simulant for nitrogen mustard adsorption studies on ZnO-based sensing materials.

In addition, oxygen enrichment of the ZnO(10 $\bar{1}$ 0) surface leads to a transition from an n-type to a p-type character, which is reversed upon adsorption of either HN₂ or DPGME. These

findings highlight the sensitivity of the ZnO electronic structure to both surface composition and molecular adsorption. Within this framework, peroxo-type oxygen adatoms emerge as plausible contributors to conductivity-type switching, providing atomistic insight into the relationship between surface defects, charge redistribution, and electronic response at oxide interfaces.

Author contributions

L. I., E. P., and C. I., DFT calculations and data curation; E. F.: conceptualization and methodology, DFT studies, funding acquisition, and writing – review and editing; G. T. project administration, methodologies, DFT studies, supervision, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information (SI): S-1. Additional computational details; S-2. Supplementary data on isolated molecules; S-3. Supplementary data on periodic models. See DOI: <https://doi.org/10.1039/d6cp01648k>.

Acknowledgements

This work has received funding from Università degli Studi dell'Insubria (Grant No. FAR2025).

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