

Are 2D non-stoichiometric materials better gas sensors? The case of metal chalcogenides.

Novel 2D TMCs for selective O₂, NO, NO₂, and nucleobase sensors

INTRO

- Due to their naturally layered structure, chemical and structural variety, high chemical stability, availability, and semiconductor properties such as acceptable band gaps and high carrier mobilities, 2D metal chalcogenides are regarded to be desirable chemical sensor materials [1-6].
- Recently plenty of novel 2D metal chalcogenide stoichiometries and crystal structures have been studied both theoretically and experimentally [7-11].
- However, the chemical sensing characteristics of many of the newer proposed materials have not yet been studied. In spite of this, their peculiar stoichiometries and crystal structures make them appealing for sensing and catalytic applications.
- In the presented study the adsorption of several gas and nucleobase molecules on novel 2D binary structures of metal (Mo, W) chalcogenides (S, Se) was carried out. As a result, review of adsorption energies, charge transfer, conductivity change, selectivity and other properties are presented and compared for novel and established 2D TMCs.

METHODS

- The geometry of each structure under consideration was optimized using DFT as implemented in VASP.
- RPBE exchange-correlation functional was used.
- Grimme corrections (DFT-D3) were applied to account for Van-der-Waals interactions.
- Ion-electron interaction was described by the augmented plane waves method (PAW) with 500 eV cutoff energy.
- The partition of the first Brillouin zone into a grid of k-points was carried out within the Monkhorst-Pack scheme with grid density of 1600 generated automatically by pymatgen.
- The minimal distance between periodic images of the molecule within the supercells was 9 Å.
- Conductivities were computed using the Boltzmann transport theory as implemented in the BoltzTraP2 code.



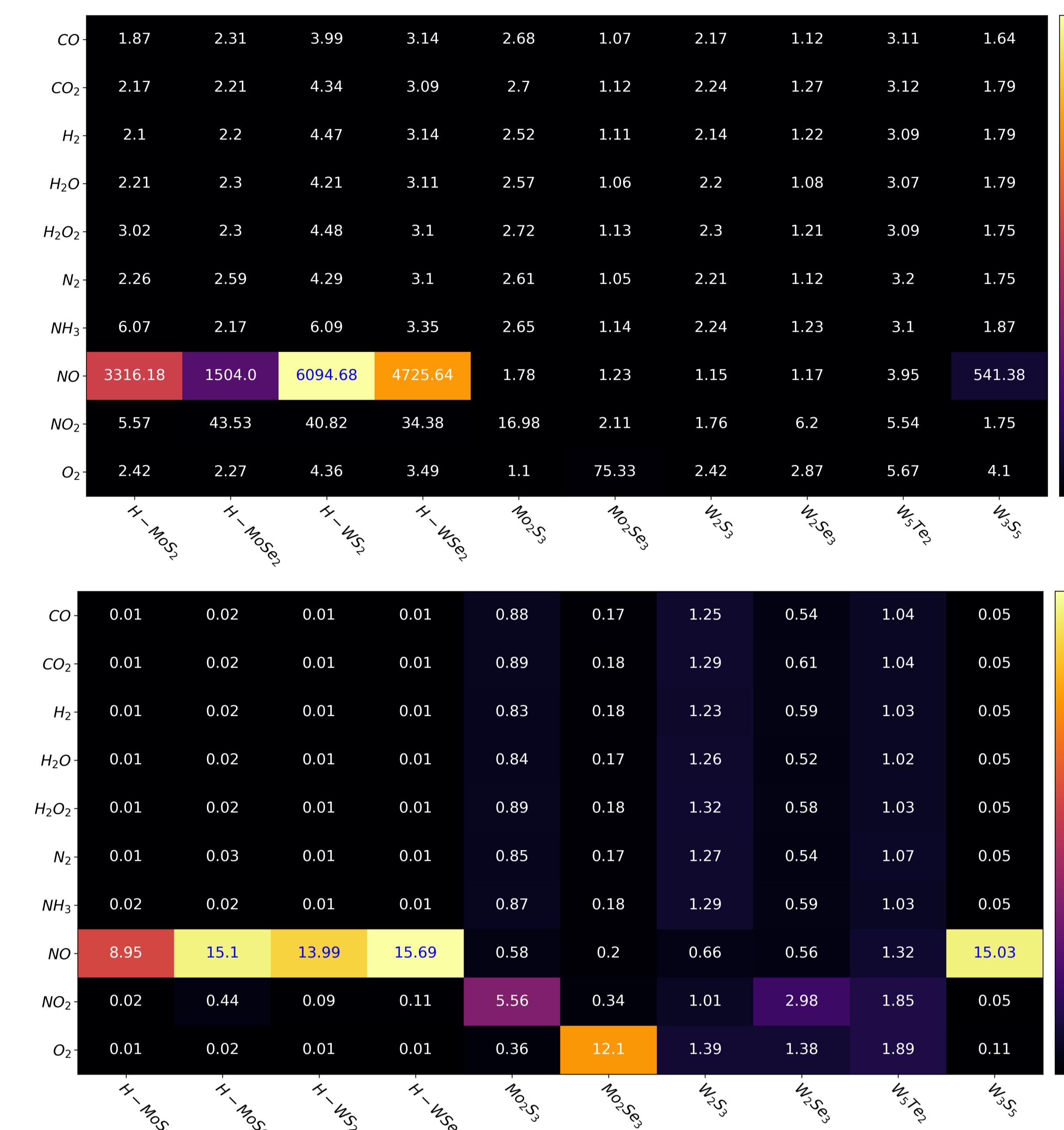
b-initio
package
simulation

USPEX Computational Materials Discovery

Boltz
TraP2

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Sensitivity for each material – molecule couple

The sensitivity of conductometric gas sensors is characterized by dimensionless parameters such as sensor signal, response ratio, or sensor response, which are defined as the ratios $S = R_d/R_g$ for reducing gases or $S = R_g/R_a$ for oxidizing gases, where R_a is the resistance of gas sensors in the reference gas (typically air) and R_g is the resistance in the reference gas containing target gases.

$$S_{m,g} = \begin{cases} \sigma_g/\sigma_0, & \text{when } g \text{ is reducing,} \\ \sigma_0/\sigma_g, & \text{when } g \text{ is oxidising.} \end{cases}$$

Selectivity for each material – molecule couple

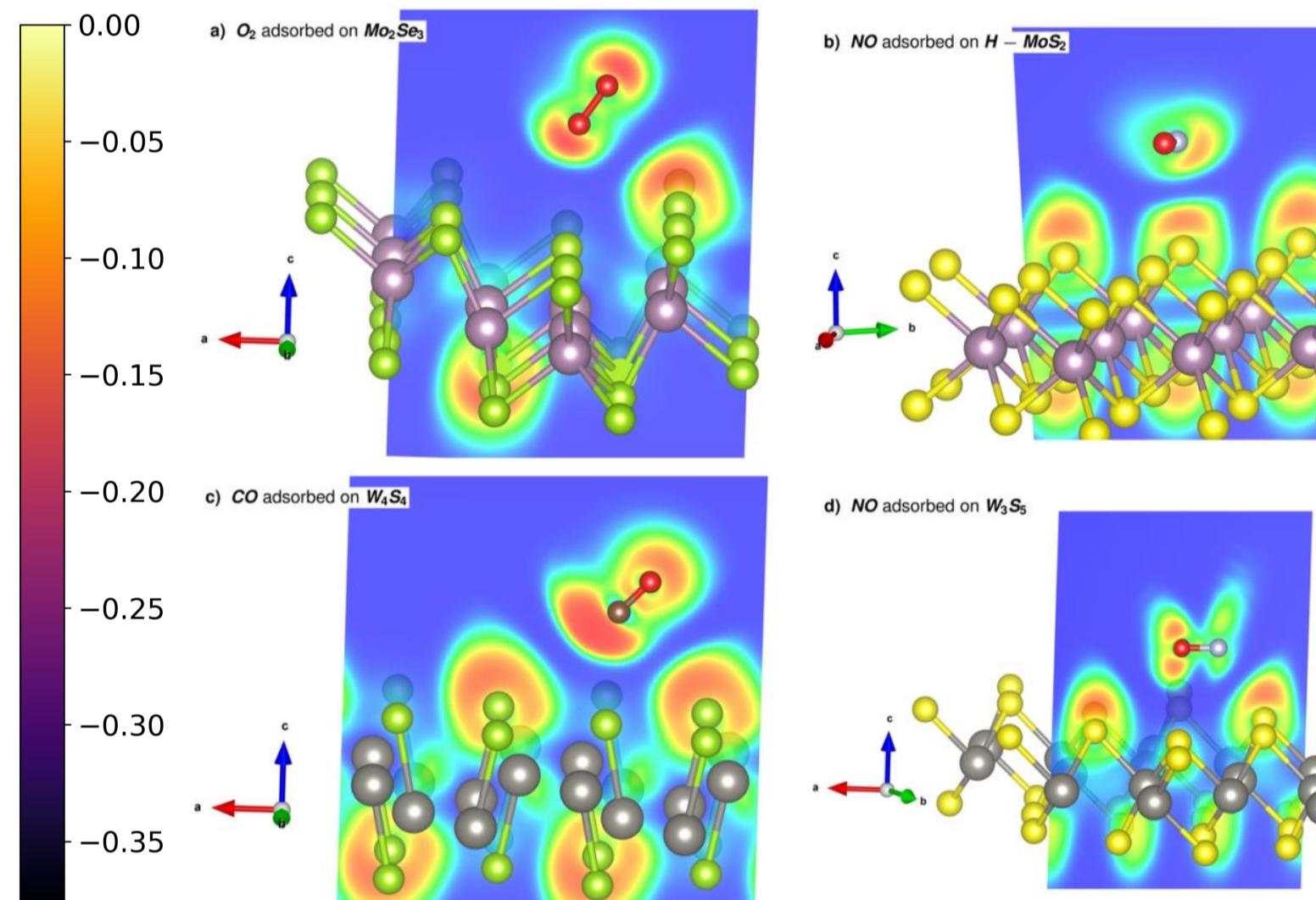
Selectivity is the capacity of a sensor to detect a particular gas in the presence of other gases. As is well known, sensors are often sensitive to many stimuli and exhibit cross-sensitivities. Thus, selectivity is a measurable quantity that may be approximated by comparing the effects of several gases on a sensor.

$$C_{m,g} = \frac{S_{m,g}}{\frac{1}{N} \sum_i^N S_{m,i}}.$$

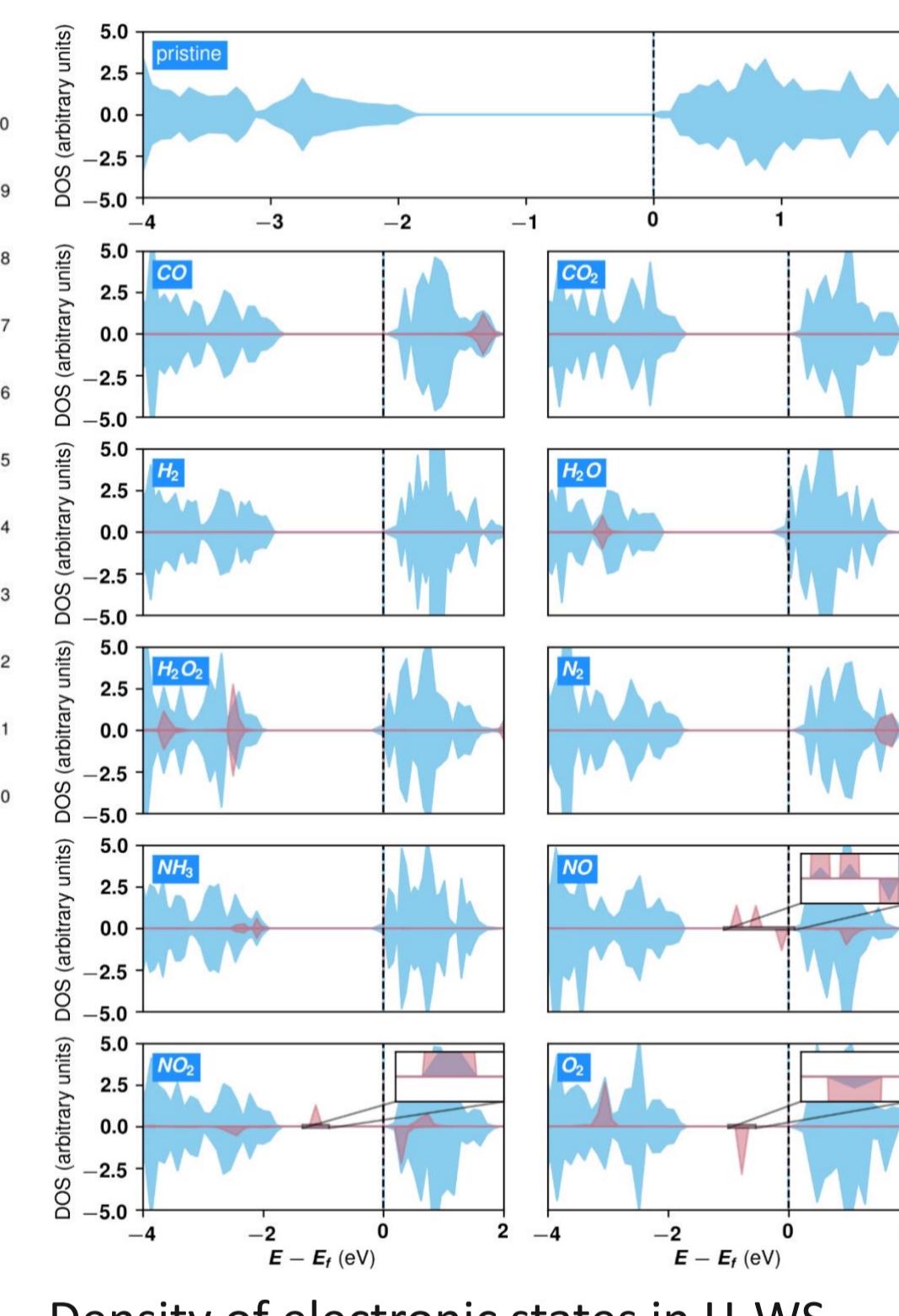
Mo₂Se₃ is the most promising material for O₂ sensing, Mo₂S₃ for NO₂ sensing, and TMDCs and W₃S₅ for NO sensing.

	CO	CO ₂	H ₂	H ₂ O	H ₂ O ₂	N ₂	NH ₃	NO	NO ₂	O ₂
CO	-0.08	-0.07	-0.08	-0.12	-0.08	-0.09	-0.1	-0.1	-0.07	-0.12
CO ₂	-0.12	-0.09	-0.13	-0.14	-0.11	-0.11	-0.12	-0.1	-0.11	-0.1
H ₂	-0.07	-0.05	-0.07	-0.09	-0.06	-0.07	-0.08	-0.07	-0.04	-0.1
H ₂ O	-0.12	-0.09	-0.11	-0.13	-0.12	-0.13	-0.13	-0.18	-0.05	-0.15
H ₂ O ₂	-0.22	-0.2	-0.22	-0.24	-0.23	-0.23	-0.2	-0.24	-0.12	-0.19
N ₂	-0.1	-0.08	-0.11	-0.12	-0.09	-0.13	-0.12	-0.14	-0.08	-0.17
NH ₃	-0.17	-0.13	-0.16	-0.21	-0.2	-0.19	-0.21	-0.2	-0.11	-0.22
NO	-0.16	-0.14	-0.17	-0.19	-0.17	-0.18	-0.17	-0.19	-0.17	-0.16
NO ₂	-0.14	-0.16	-0.15	-0.23	-0.2	-0.21	-0.21	-0.3	-0.38	-0.19
O ₂	-0.06	-0.04	-0.04	-0.05	-0.05	-0.07	-0.07	-0.09	0.0	-0.07

Calculated adsorption energies in electron-Volts.



Electron localization function for the following adsorption configurations: a) O₂ molecule adsorbed on Mo₂Se₃, b) NO adsorbed on H-MoS₂, c) CO adsorbed on W₄S₄, and d) NO adsorbed on W₃S₅.



Density of electronic states in H-WS₂ without and with the presence of adsorbed molecules. By blue and red are illustrated the contributions from the monolayer and the molecules respectively. The Fermi level is shifted to zero.

All gas adsorption energies on considered semiconducting 2D materials are less than 0.4 eV in absolute value. Combined with charge transfer and electron localization function analysis one can conclude that the interaction in adsorbed configurations is of mainly Van-der-Waals character.

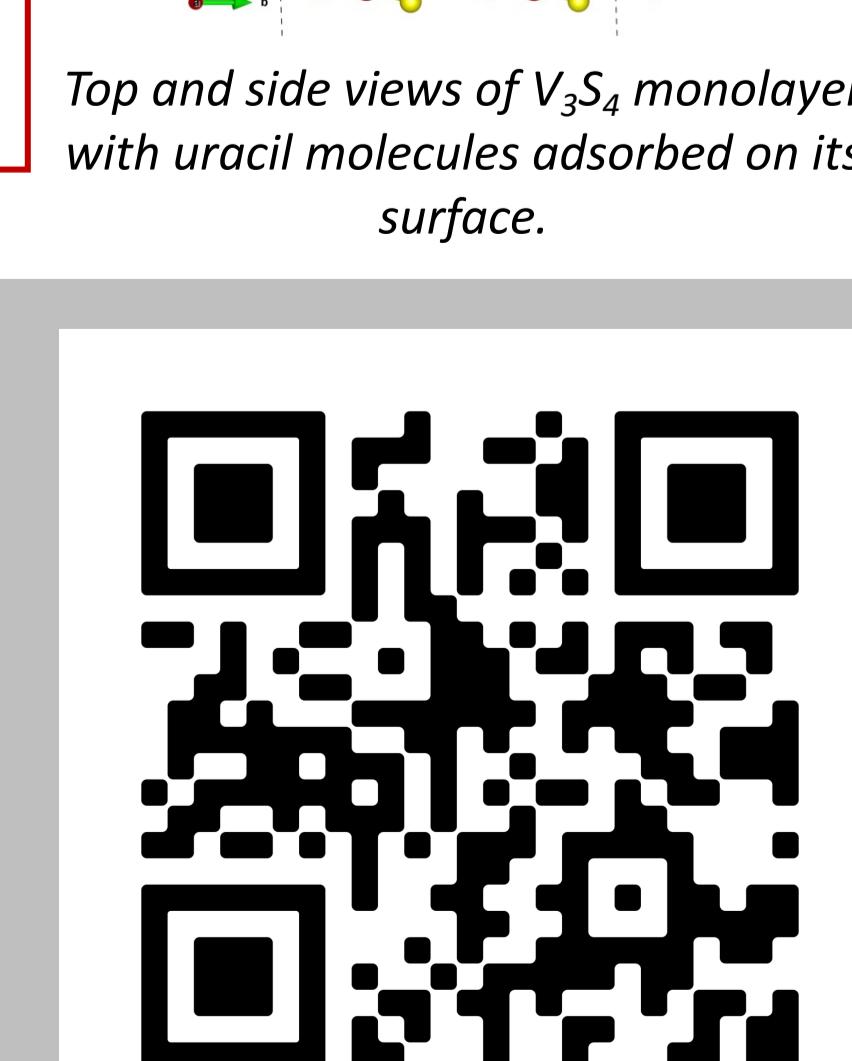
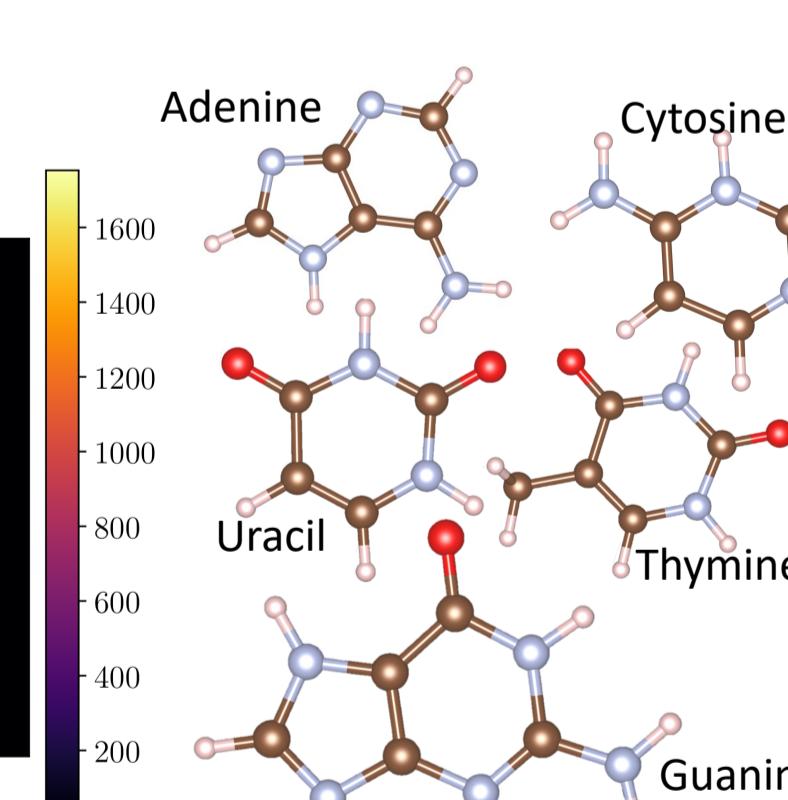


Calculated adsorption energies in electron-Volts.



Sensitivity for each material – nucleobase couple

- H-MoS₂ and H-WS₂ considerably change conductivity when guanine is adsorbed, making them appropriate for the selective identification of guanine.
- In addition, H-MoS₂ has a substantially greater sensitivity towards cytosine than H-WS₂, allowing these two materials to be combined in devices that selectively and consistently detect guanine and cytosine.
- V₃S₄ modifies its conductivity in the presence of adsorbed nucleobases, making it appropriate for nucleobase sensing without categorization since it lacks considerable selectivity.



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