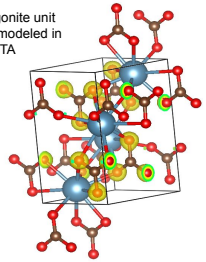
Density Functional Theory and Small Molecule-Protonated Aragonite Surface Interactions as Applied to Cultural Heritage

Layla S. Huff,[1] M. Kaylor Stroot,[2] Xavier J. Welch,[1] Marcus L. Wilson,[3] Jessica E. Heimann,[4] and Joseph W. Bennett[4]
Morgan State University,[1] McDaniel College,[2] Towson University,[3] and University of Maryland Baltimore County[4]

Introduction

Aragonite unit cell modeled in VESTA



Aragonite. Image © Index Open.

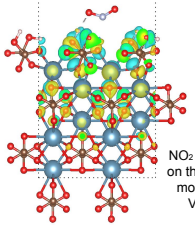
- Aragonite is a stable form of calcium carbonate ($CaCO_3$) that occurs at high pressures
- It is found in stalactites, ore minerals, sediments, shells, coral, and pearls and is used in historical pigments, paints, and stone used in sculptures (e.g. limestone)
- Small molecules (adsorbates) can exacerbate the degradation of materials
- Major outdoor pollutants are acidic particulates and marine aerosols
- It is valuable to study the interactions between an aragonite surface and selected adsorbates
- Adsorption energy is a quantitative value that describes the strength of the interactions and provides information on how destructive different adsorbates can be
- Conservators and conservation scientists work towards understanding the science behind a work of art
- Conservators then create and carry out treatment plans based on scientific knowledge

Project Goals

To identify, model, and examine possible pollutants (adsorbates) and their interactions with a protonated aragonite surface

Methods

NO_2 molecule modeled in XCrySDen

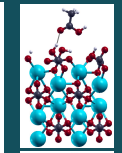


NO_2 molecule on the surface modeled in VESTA

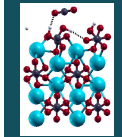
All calculations described here employ periodic DFT methods (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and are carried out using Quantum Espresso, an open source software package (Giannozzi et al., 2009; Giannozzi et al., 2017). All atoms are represented using GBRV-type ultrasoft pseudopotentials (Vanderbilt, 1990; Garrity et al., 2014). A plane-wave cutoff of 40 Ry and charge density cutoff of 320 Ry are employed for all calculations, in line with similar surface studies (Bennett, Jones, Hamers, et al., 2018; Bennett, Jones, Huang, et al., 2018; Bennett et al., 2020). Bulk structural relaxations use a 6x6x6 k-point grid (Monkhorst and Pack, 1976), and the convergence criteria for self-consistent relaxations is $5x10^{-6}$ eV. Geometry optimization of all surface-adsorbate interactions did not include fixing any layers, as detailed in Corum et al. (2017) where all atoms are free to relax. All calculations are performed at the GGA level using the Wu-Cohen (WC) modified PBE-GGA exchange correlation functional for solids (Perdew et al., 1996; Wu and Cohen, 2006).

Results & Discussion

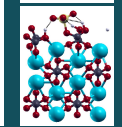
Adsorbate	Configuration	E_a (kcal/mol)	E_a (eV)
CH_3COOH	1	4.13	0.179
NO_2	-	2.39	0.104
CH_2O	1	1.36	0.059
CH_4	-	-0.69	-0.030
CF_4	-	-0.80	-0.035
$CH_2C(CH_3)_2$	-	-1.67	-0.072
CF_3COCF_3	-	-3.63	-0.158
O_3	-	-5.01	-0.217
CF_3COOH	-	-5.32	-0.231
CF_3COCH_3	-	-5.89	-0.255
CO_2	-	-6.31	-0.274
CH_3COOH	2	-9.28	-0.403
H_2S	-	-13.79	-0.598
HCOOH	2	-14.32	-0.621
SO_2	-	-14.82	-0.643
CH_2O	2	-15.61	-0.677
CH_3CHO	-	-16.37	-0.710
CH_3COCH_3	-	-18.02	-0.781
HCOOH	1	-18.89	-0.819
H_2O	-	-28.30	-1.227
CF_3OH	-	-31.47	-1.364
H_2SO_4	-	-32.78	-1.422
CH_3OH	-	-34.93	-1.515
SO_3	-	-47.12	-2.043



CH_3COOH (C1) molecule on the surface modeled in XCrySDen **(E_a = 0.179 eV)**

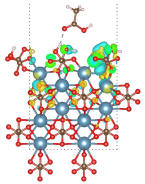


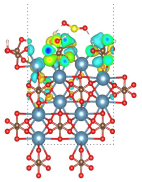
CO_2 molecule on the surface modeled in XCrySDen **(E_a = -0.274 eV)**



SO_3 molecule on the surface modeled in XCrySDen **(E_a = -2.043 eV)**

Charge density difference plots of CH_3COOH (C1) (left) and SO_3 (right) on the surface modeled in VESTA

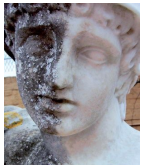




The yellow color represents positive charge density (i.e. more charge density when the adsorbate is present), and the blue color represents negative charge density (i.e. more charge density when the adsorbate is not present)

Conclusions

- DFT was used to analyze the interactions of small molecule adsorbates and atmospheric pollutants on a protonated aragonite surface
- Low humidity environments should be maintained to avoid the detrimental effects of water on $CaCO_3$
- Air filters in museums should specifically target sulfur-containing compounds to eliminate SO_2, SO_3, or H_2SO_4
- Fluorinated compounds are generally weaker adsorbates than their non-fluorinated counterparts; however, their negative environmental impacts should not be ignored
- Future iterations of this program may work with additional configurations of adsorbates or larger adsorbates related to conservation such as citric acid



Wedjat Eye Amulet, Egypt,1070–664 B.C. (Third Intermediate Period), Aragonite, The Metropolitan Museum of Art, New York

"Eroded Marble Garden Statuary" - Half cleaned using a controlled nebulous spray system. Building Conservation.com

References

Gettens, R.J., Fitzhugh, E.W., Feller, R.L., 1974. Calcium Carbonate Whites. *Studies in Conservation* 19 (3), 157–184.

Corvo, F., Reyes-Trujeque, J., Valdés, C., Villaseñor, F., Cuesta, O., Aguilar, D., Quintana, P., 2010. Influence of air pollution and humidity on limestone materials degradation in historical buildings located in cities under tropical coastal climates. *Water, Air, and Soil Pollution* 205, 359-375.

Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev.* 136 (3B), B864-B871.

Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140 (4A), A1133-A1138.

Giannozzi, P., *et al.* 2017. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys.-Condens. Mat.* 29 (46), 465901.

Giannozzi, P., *et al.*, 2009. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.-Condens. Mat.* 21 (39), 395502.

Vanderbilt, D., 1990. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* 41 (11), 7892-7895.

Garrity, K.F., Bennett, J.W., Rabe, K.M., Vanderbilt, D., 2014. Pseudopotentials for high-throughput DFT calculations. *Comp. Mater. Sci.* 81, 446-452.

Bennett, J.W., Jones, D.T., Hamers, R.J., Mason, S.E., 2018. First-principles and thermodynamics study of compositionally tuned complex metal oxides: Cation release from the (001) surface of Mn-rich lithium nickel manganese cobalt oxide. Inorg. Chem. 57 (21), 13300-13311.

Bennett, J.W., Jones, D., Huang, X., Hamers, R.J., Mason, S.E., 2018. Dissolution of complex metal oxides from first-principles and thermodynamics: Cation removal from the (001) Surface of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$. Environ. Sci. Technol. 52 (10), 5792-5802.

Bennett, J.W., *et al.* 2020. Emerging investigator series: first-principles and thermodynamics comparison of compositionally-tuned delafossites: cation release from the (001) surface of complex metal oxides.

Monkhorst, H.J., Pack, J.D., 1976. Special points for Brillouin-zone integrations. Phys. Rev. B 13 (12), 5188-5192.

Corum, K.W., Huang, X., Bennett, J.W., Mason, S.E., 2017. Systematic density functional theory study of the structural and electronic properties of constrained and fully relaxed (0 0 1) surfaces of alumina and hematite. Mol. Simulat. 43 (5-6), 406-419.

Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. Phys. Rev. Lett. 77 (18), 3865-3868.

Wu, Z., Cohen, R.E., 2006. More accurate generalized gradient approximation for solids. Phys. Rev. B 73 (23), 235116.

Acknowledgements

This work was performed as part of the Baltimore SCIART Program, which is supported by the Andrew W. Mellon Foundation under Award 41500634. Additional funding was provided by the XSEDE start-up grant TG-CHE190075 and renewal allocation TG-CHE200108, which are supported by NSF grant number ACI-1548562. All calculations were performed using the UMBC HPCF. The acquisition of equipment for the HPCF is partially supported by the NSF, whose support we gratefully acknowledge and which requires the following notice: This material is based upon work supported by the NSF under the MRI grants CNS-0821258, CNS-1228778, and OAC-1726023, and the SCREMS grant DMS-0821311. Special thanks to Dr. Rosenzweig for your support. Thank you to all the speakers and special guests for your time and expertise!