

- [157] W Arbelo-González, R Crespo-Otero and M Barbatti, “Steady and Time-Resolved Photoelectron Spectra Based on Nuclear Ensembles”, *J Chem Theory Comput*, 2016, **12**, 5037–5049, DOI: 10.1021/acs.jctc.6b00704.
- [158] M Barbatti, A J A Aquino and H Lischka, “The UV absorption of nucleobases: semi-classical ab initio spectra simulations”, *Phys Chem Chem Phys*, 2010, **12**, 4959, DOI: 10.1039/b924956g.
- [159] L E de Sousa and P de Silva, “Photophysics of Solvated Molecules: Computational Protocol Combining Nuclear Ensemble and Nonequilibrium State-Specific Solvation Methods”, *J Phys Chem A*, 2023, **127**, 8200–8208, DOI: 10.1021/acs.jpca.3c03533.
- [160] A D McLachlan and M A Ball, “Time-Dependent Hartree–Fock Theory for Molecules”, *Rev Mod Phys*, 1964, **36**, 844–855, DOI: 10.1103/RevModPhys.36.844.
- [161] E Runge and E K U Gross, “Density-Functional Theory for Time-Dependent Systems”, *Phys Rev Lett*, 1984, **52**, 997–1000, DOI: 10.1103/PhysRevLett.52.997.
- [162] E K U Gross and W Kohn, “Time-Dependent Density-Functional Theory”, in *Density Functional Theory of Many-Fermion Systems*, ed P-O Löwdin, Academic Press, 1990, vol 21, pp 255–291, DOI: 10.1016/S0065-3276(08)60600-0.
- [163] S K Ghosh and A K Dhara, “Density-functional theory of many-electron systems subjected to time-dependent electric and magnetic fields”, *Phys Rev A*, 1988, **38**, 1149–1158, DOI: 10.1103/PhysRevA.38.1149.
- [164] R van Leeuwen, “Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory”, *Phys Rev Lett*, 1999, **82**, 3863–3866, DOI: 10.1103/PhysRevLett.82.3863.
- [165] E K U Gross, J F Dobson and M Petersilka, “Density functional theory of time-dependent phenomena”, in *Density Functional Theory II: Relativistic and Time Dependent Extensions*, ed R F Nalewajski, Springer Berlin Heidelberg, Berlin, Heidelberg, 1996, pp 81–172, DOI: 10.1007/BFb0016643.
- [166] R van Leeuwen, “Causality and Symmetry in Time-Dependent Density-Functional Theory”, *Phys Rev Lett*, 1998, **80**, 1280–1283, DOI: 10.1103/PhysRevLett.80.1280.
- [167] M E Casida, “Time-Dependent Density Functional Response Theory for Molecules”, in *Recent Advances in Density Functional Methods*, pp 155–192, DOI: 10.1142/9789812830586_0005.
- [168] *Fundamentals of Time-Dependent Density Functional Theory*, ed M A L Marques, N T Maitra, F M S Nogueira, E K U Gross and A Rubio, Springer, Heidelberg, Germany, 1st ed, 2012, DOI: 10.1007/978-3-642-23518-4.
- [169] S Hirata and M Head-Gordon, “Time-dependent density functional theory within the Tamm–Dancoff approximation”, *Chem Phys Lett*, 1999, **314**, 291–299, DOI: 10.1016/S0009-2614(99)01149-5.
- [170] S Grimme and F Neese, “Double-hybrid density functional theory for excited electronic states of molecules”, *J Chem Phys*, 2007, **127**, 154116, DOI: 10.1063/1.2772854.

- [171] M Casanova-Páez and L Goerigk, “Assessing the Tamm–Dancoff approximation, singlet–singlet, and singlet–triplet excitations with the latest long-range corrected double-hybrid density functionals”, *J Chem Phys*, 2020, **153**, 064106, DOI: 10.1063/5.0018354.
- [172] A Chantzis, A D Laurent, C Adamo and D Jacquemin, “Is the Tamm–Dancoff Approximation Reliable for the Calculation of Absorption and Fluorescence Band Shapes?”, *J Chem Theory Comput*, 2013, **9**, 4517–4525, DOI: 10.1021/ct400597f.
- [173] T Rangel, S M Hamed, F Bruneval and J B Neaton, “An assessment of low-lying excitation energies and triplet instabilities of organic molecules with an ab initio Bethe–Salpeter equation approach and the Tamm–Dancoff approximation”, *J Chem Phys*, 2017, **146**, 194108, DOI: 10.1063/1.4983126. 
- [174] F W Byron and R W Fuller, *Mathematics of Classical and Quantum Physics*, Dover, New York, NY, USA, 1992.
- [175] R McWeeny, *Methods of Molecular Quantum Mechanics*, Academic Press, London, UK, 2nd ed, 1989.
- [176] M Nooijen and R J Bartlett, “Similarity transformed equation-of-motion coupled-cluster theory: Details, examples, and comparisons”, *J Chem Phys*, 1997, **107**, 6812–6830, DOI: 10.1063/1.474922.
- [177] F Neese, A Hansen and D G Liakos, “Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis”, *J Chem Phys*, 2009, **131**, 064103, DOI: 10.1063/1.3173827.
- [178] C Riplinger and F Neese, “An efficient and near linear scaling pair natural orbital based local coupled cluster method”, *J Chem Phys*, 2013, **138**, 034106, DOI: 10.1063/1.4773581.
- [179] C Riplinger, B Sandhoefer, A Hansen and F Neese, “Natural triple excitations in local coupled cluster calculations with pair natural orbitals”, *J Chem Phys*, 2013, **139**, 134101, DOI: 10.1063/1.4821834.
- [180] A K Dutta, F Neese and R Izsák, “Towards a pair natural orbital coupled cluster method for excited states”, *J Chem Phys*, 2016, **145**, 034102, DOI: 10.1063/1.4958734.
- [181] J Kussmann, M Beer and C Ochsenfeld, “Linear-scaling self-consistent field methods for large molecules”, *WIREs Comput Mol Sci*, 2013, **3**, 614–636, DOI: 10.1002/wcms.1138.
- [182] C Ochsenfeld, J Kussmann and D S Lambrecht, “Linear-Scaling Methods in Quantum Chemistry”, in *Reviews in Computational Chemistry*, ed K B Lipkowitz and T R Cundari, John Wiley & Sons, Inc, Hoboken, New Jersey, 2007, vol 23, chap 1, pp 1–82, DOI: 10.1002/9780470116449.ch1.
- [183] S Goedecker, “Linear scaling electronic structure methods”, *Rev Mod Phys*, 1999, **71**, 1085–1123, DOI: 10.1103/RevModPhys.71.1085.
- [184] G E Scuseria, “Linear Scaling Density Functional Calculations with Gaussian Orbitals”, *J Phys Chem A*, 1999, **103**, 4782–4790, DOI: 10.1021/jp990629s.

- [185] C Fonseca Guerra, J G Snijders, G te Velde and E J Baerends, “Towards an order-N DFT method”, *Theor Chem Acc*, 1998, **99**, 391–403, DOI: 10.1007/s002140050353.
- [186] S Mohr, L E Ratcliff, L Genovese, D Caliste, P Boulanger, S Goedecker and T Deutsch, “Accurate and efficient linear scaling DFT calculations with universal applicability”, *Phys Chem Chem Phys*, 2015, **17**, 31360–31370, DOI: 10.1039/C5CP00437C.
- [187] M S Gordon, D G Fedorov, S R Pruitt and L V Slipchenko, “Fragmentation Methods: A Route to Accurate Calculations on Large Systems”, *Chem Rev*, 2012, **112**, 632–672, DOI: 10.1021/cr200093j.
- [188] K Raghavachari and A Saha, “Accurate Composite and Fragment-Based Quantum Chemical Models for Large Molecules”, *Chem Rev*, 2015, **115**, 5643–5677, DOI: 10.1021/cr500606e.
- [189] B Wang, K R Yang, X Xu, M Isegawa, H R Leverentz and D G Truhlar, “Quantum Mechanical Fragment Methods Based on Partitioning Atoms or Partitioning Coordinates”, *Acc Chem Res*, 2014, **47**, 2731–2738, DOI: 10.1021/ar500068a.
- [190] S Verma, A Mitra, Q Wang, R D’Cunha, B Jangid, M R Hennefarth, V Agarawal, L Otis, S Halder, M R Hermes and L Gagliardi, “Multireference Embedding and Fragmentation Methods for Classical and Quantum Computers: From Model Systems to Realistic Applications”, *Chem Rev*, 2026, **126**, 184–203, DOI: 10.1021/acs.chemrev.5c00486.
- [191] Q Sun and G K-L Chan, “Quantum Embedding Theories”, *Acc Chem Res*, 2016, **49**, 2705–2712, DOI: 10.1021/acs.accounts.6b00356.
- [192] L O Jones, M A Mosquera, G C Schatz and M A Ratner, “Embedding Methods for Quantum Chemistry: Applications from Materials to Life Sciences”, *J Am Chem Soc*, 2020, **142**, 3281–3295, DOI: 10.1021/jacs.9b10780.
- [193] M Liu, Y Wang, Y Chen, M J Field and J Gao, “QM/MM through the 1990s: The First Twenty Years of Method Development and Applications”, *Isr J Chem*, 2014, **54**, 1250–1263, DOI: 10.1002/ijch.201400036.
- [194] H Lin and D G Truhlar, “QM/MM: what have we learned, where are we, and where do we go from here?”, *Theor Chem Acc*, 2007, **117**, 185–199, DOI: 10.1007/s00214-006-0143-z.
- [195] S Pezeshki and H Lin, “Recent developments in QM/MM methods towards open-boundary multi-scale simulations”, *Mol Simul*, 2015, **41**, 168–189, DOI: 10.1080/08927022.2014.911870.
- [196] J Ho, H Yu, Y Shao, M Taylor and J Chen, “How Accurate Are QM/MM Models?”, *J Phys Chem A*, 2025, **129**, 1517–1528, DOI: 10.1021/acs.jpca.4c06521.
- [197] E Boulanger and J N Harvey, “QM/MM methods for free energies and photochemistry”, *Curr Opin Struct Biol*, 2018, **49**, 72–76, DOI: 10.1016/j.sbi.2018.01.003.
- [198] P M Morse, “Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels”, *Phys Rev*, 1929, **34**, 57–64, DOI: 10.1103/PhysRev.34.57.
- [199] B R Brooks, R E Bruccoleri, B D Olafson, D J States, S Swaminathan and M Karplus, “CHARMM: A program for macromolecular energy, minimization, and dynamics calculations”, *J Comput Chem*, 1983, **4**, 187–217, DOI: 10.1002/jcc.540040211.

- [200] F A Momany and R Rone, "Validation of the general purpose QUANTA ®3.2/CHARMm® force field", *J Comput Chem*, 1992, **13**, 888–900, DOI: 10.1002/jcc.540130714.
- [201] B R Brooks, C L Brooks III, A D Mackerell Jr, L Nilsson, R J Petrella, B Roux, Y Won, G Archontis, C Bartels, S Boresch, A Caflisch, L Caves, Q Cui, A R Dinner, M Feig, S Fischer, J Gao, M Hodoscek, W Im, K Kuczera, T Lazaridis, J Ma, V Ovchinnikov, E Paci, R W Pastor, C B Post, J Z Pu, M Schaefer, B Tidor, R M Venable, H L Woodcock, X Wu, W Yang, D M York and M Karplus, "CHARMM: The biomolecular simulation program", *J Comput Chem*, 2009, **30**, 1545–1614, DOI: 10.1002/jcc.21287.
- [202] J Huang and A D MacKerell Jr, "CHARMM36 all-atom additive protein force field: Validation based on comparison to NMR data", *J Comput Chem*, 2013, **34**, 2135–2145, DOI: 10.1002/jcc.23354.
- [203] J D Jackson, *Classical Electrodynamics*, John Wiley, New York, NY, USA, 3rd ed, 1999.
- [204] Z Jing, C Liu, S Y Cheng, R Qi, B D Walker, J-P Piquemal and P Ren, "Polarizable Force Fields for Biomolecular Simulations: Recent Advances and Applications", *Annu Rev Biophys*, 2019, **48**, 371–394, DOI: 10.1146/annurev-biophys-070317-033349. 
- [205] C M Baker, "Polarizable force fields for molecular dynamics simulations of biomolecules", *WIREs Comput Mol Sci*, 2015, **5**, 241–254, DOI: 10.1002/wcms.1215.
- [206] J A Lemkul, J Huang, B Roux and A D MacKerell Jr, "An Empirical Polarizable Force Field Based on the Classical Drude Oscillator Model: Development History and Recent Applications", *Chem Rev*, 2016, **116**, 4983–5013, DOI: 10.1021/acs.chemrev.5b00505. 
- [207] S Patel and C L Brooks III, "CHARMM fluctuating charge force field for proteins: I parameterization and application to bulk organic liquid simulations", *J Comput Chem*, 2004, **25**, 1–16, DOI: 10.1002/jcc.10355.
- [208] J E Davis and S Patel, "Charge Equilibration Force Fields for Lipid Environments: Applications to Fully Hydrated DPPC Bilayers and DMPC-Embedded Gramicidin A", *J Phys Chem B*, 2009, **113**, 9183–9196, DOI: 10.1021/jp901088g.
- [209] P Dauber-Osguthorpe and A T Hagler, "Biomolecular force fields: where have we been, where are we now, where do we need to go and how do we get there?", *J Comput-Aided Mol Des*, 2019, **33**, 133–203, DOI: 10.1007/s10822-018-0111-4.
- [210] B Soczó and I Pethes, "Comparison of water models for structure prediction", *J Mol Liq*, 2025, **433**, 127975, DOI: 10.1016/j.molliq.2025.127975. 
- [211] K Vanommeslaeghe, E Hatcher, C Acharya, S Kundu, S Zhong, J Shim, E Darian, O Guvench, P Lopes, I Vorobyov and A D Mackerell Jr, "CHARMM general force field: A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields", *J Comput Chem*, 2010, **31**, 671–690, DOI: 10.1002/jcc.21367.
- [212] K Vanommeslaeghe and A D MacKerell Jr, "Automation of the CHARMM General Force Field (CGenFF) I: Bond Perception and Atom Typing", *J Chem Inf Model*, 2012, **52**, 3144–3154, DOI: 10.1021/ci300363c.

- [213] K Vanommeslaeghe, E P Raman and A D MacKerell Jr, "Automation of the CHARMM General Force Field (CGenFF) II: Assignment of Bonded Parameters and Partial Atomic Charges", *J Chem Inf Model*, 2012, **52**, 3155–3168, DOI: 10.1021/ci3003649.
- [214] V Zoete, M A Cuendet, A Grosdidier and O Michielin, "SwissParam: A fast force field generation tool for small organic molecules", *J Comput Chem*, 2011, **32**, 2359–2368, DOI: 10.1002/jcc.21816.
- [215] M Bugnon, M Goullieux, U F Röhrig, M A S Perez, A Daina, O Michielin and V Zoete, "SwissParam 2023: A Modern Web-Based Tool for Efficient Small Molecule Parametrization", *J Chem Inf Model*, 2023, **63**, 6469–6475, DOI: 10.1021/acs.jcim.3c01053.
- [216] Worldwide Protein Data Bank, *Atomic Coordinate Entry Format Version 3.3*, Worldwide Protein Data Bank, 2012, <https://www.wwpdb.org/documentation/file-format-content/format33/sect1.html>.
- [217] H Berman, K Henrick and H Nakamura, "Announcing the worldwide Protein Data Bank", *Nat Struct Mol Biol*, 2003, **10**, 980–980, DOI: 10.1038/nsb1203-980.
- [218] G B Sushko, I A Solov'yov, A V Verkhovtsev, S N Volkov and A V Solov'yov, "Studying chemical reactions in biological systems with MBN Explorer: implementation of molecular mechanics with dynamical topology", *Eur Phys J D*, 2016, **70**, 12, DOI: 10.1140/epjd/e2015-60424-9.
- [219] A C T van Duin, S Dasgupta, F Lorant and W A Goddard, "ReaxFF: A reactive force field for hydrocarbons", *J Phys Chem A*, 2001, **105**, 9396–9409, DOI: 10.1021/jp004368u.
- [220] T P Senftle, S Hong, M M Islam, S B Kylasa, Y Zheng, Y K Shin, C Junkermeier, R Engel-Herbert, M J Janik, H M Aktulga, T Verstraelen, A Grama and A C T van Duin, "The ReaxFF reactive force-field: development, applications and future directions", *npj Comput Mater*, 2016, **2**, 15011, DOI: 10.1038/npjcompumats.2015.11.
- [221] G B Sushko, I A Solov'yov and A V Solov'yov, "Molecular dynamics for irradiation driven chemistry: application to the FEBID process", *Eur Phys J D*, 2016, **70**, 217, DOI: 10.1140/epjd/e2016-70283-5.
- [222] P de Vera, M Azzolini, G Sushko, I Abril, R Garcia-Molina, M Dapor, I A Solov'yov and A V Solov'yov, "Multiscale simulation of the focused electron beam induced deposition process", *Sci Rep*, 2020, **10**, 20827, DOI: 10.1038/s41598-020-77120-z.
- [223] A Prosvetov, A V Verkhovtsev, G Sushko and A V Solov'yov, "Irradiation-driven molecular dynamics simulation of the FEBID process for Pt(PF₃)₄", *Beilstein J Nanotechnol*, 2021, **12**, 1151–1172, DOI: 10.3762/bjnano.12.86.
- [224] A Prosvetov, A V Verkhovtsev, G Sushko and A V Solov'yov, "Atomistic simulation of the FEBID-driven growth of iron-based nanostructures", *Phys Chem Chem Phys*, 2022, **24**, 10807–10819, DOI: 10.1039/D2CP00809B.
- [225] A Prosvetov, A V Verkhovtsev, G Sushko and A V Solov'yov, "Atomistic modeling of thermal effects in focused electron beam-induced deposition of Me₂Au(tfac)", *Eur Phys J D*, 2023, **77**, 15, DOI: 10.1140/epjd/s10053-023-00598-5.

- [226] H Lyshchuk, A V Verkhovtsev, J Kočišek, J Fedor and A V Solov'yov, "Release of Neutrals in Electron-Induced Ligand Separation from MeCpPtMe₃: Theory Meets Experiment", *J Phys Chem A*, 2025, **129**, 2016–2023, DOI: 10.1021/acs.jpca.4c08259. 
- [227] S W de Leeuw, J W Perram and E R Smith, "Simulation of electrostatic systems in periodic boundary conditions. I. Lattice sums and dielectric constants", *Proc R Soc Lond A Math Phys Sci*, 1980, **373**, 27–56, DOI: 10.1098/rspa.1980.0135.
- [228] P P Ewald, "Die Berechnung optischer und elektrostatischer Gitterpotentiale", *Ann Phys (Berlin)*, 1921, **369**, 253–287, DOI: 10.1002/andp.19213690304.
- [229] J W Eastwood, R W Hockney and D N Lawrence, "P₃M₃DP–The three-dimensional periodic particle-particle/ particle-mesh program", *Comput Phys Commun*, 1980, **19**, 215–261, DOI: 10.1016/0010-4655(80)90052-1.
- [230] R Hockney and J Eastwood, *Computer Simulation Using Particles*, CRC Press, Boca Raton, FL, 1st ed, 1988, DOI: 10.1201/9780367806934.
- [231] T Darden, D York and L Pedersen, "Particle mesh Ewald: An $N \cdot \log(N)$ method for Ewald sums in large systems", *J Chem Phys*, 1993, **98**, 10089–10092, DOI: 10.1063/1.464397.
- [232] U Essmann, L Perera, M L Berkowitz, T Darden, H Lee and L G Pedersen, "A smooth particle mesh Ewald method", *J Chem Phys*, 1995, **103**, 8577–8593, DOI: 10.1063/1.470117.
- [233] M Deserno and C Holm, "How to mesh up Ewald sums. I. A theoretical and numerical comparison of various particle mesh routines", *J Chem Phys*, 1998, **109**, 7678–7693, DOI: 10.1063/1.477414.
- [234] A Y Toukmaji and J A Board, "Ewald summation techniques in perspective: a survey", *Comput Phys Commun*, 1996, **95**, 73–92, DOI: 10.1016/0010-4655(96)00016-1.
- [235] D Frenkel and B Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, London, UK, 3rd ed, 2023, DOI: 10.1016/B978-0-12-267351-1.X5000-7.
- [236] H J C Berendsen, *Simulating the Physical World: Hierarchical Modeling from Quantum Mechanics to Fluid Dynamics*, Cambridge University Press, Cambridge, MA, USA, 2007, DOI: 10.1017/CB09780511815348.
- [237] B Leimkuhler and C Matthews, *Molecular Dynamics: With Deterministic and Stochastic Numerical Methods*, Springer, Cham, 1st ed, 2015, vol 39, DOI: 10.1007/978-3-319-16375-8.
- [238] M Tuckerman, B J Berne and G J Martyna, "Reversible multiple time scale molecular dynamics", *J Chem Phys*, 1992, **97**, 1990–2001, DOI: 10.1063/1.463137.
- [239] Störmer, C., "Sur les trajectoires des corpuscules électrisés dans l'espace sous l'action du magnétisme terrestre, avec application aux aurores boréales", *Radium (Paris)*, 1912, **9**, 395–399, DOI: 10.1051/radium:01912009011039501.
- [240] L Verlet, "Computer 'Experiments' on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules", *Phys Rev*, 1967, **159**, 98–103, DOI: 10.1103/PhysRev.159.98. 

- [241] W C Swope, H C Andersen, P H Berens and K R Wilson, "A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters", *J Chem Phys*, 1982, **76**, 637–649, DOI: 10.1063/1.442716.
- [242] J Snyman, "A new and dynamic method for unconstrained minimization", *Appl Math Model*, 1982, **6**, 449–462, DOI: 10.1016/S0307-904X(82)80007-3. 
- [243] M Hestenes and E Stiefel, "Methods of conjugate gradients for solving linear systems", *J Res Nat Bur Standards*, 1952, **49**, 409–436.
- [244] E Polak and G Ribiere, "Note sur la convergence de méthodes de directions conjuguées", *Rev Fr Inform Rech Opér Sér Rouge*, 1969, **3**, 35–43.
- [245] B Polyak, "The conjugate gradient method in extremal problems", *USSR Comput Math Math Phys*, 1969, **9**, 94–112, DOI: 10.1016/0041-5553(69)90035-4.
- [246] L N Trefethen and D Bau III, *Numerical Linear Algebra*, SIAM, Philadelphia, PA, USA, 1997.
- [247] J Nocedal and S Wright, *Numerical Optimization*, Springer, New York, NY, USA, 2nd ed, 2006, DOI: 10.1007/978-0-387-40065-5.
- [248] H J C Berendsen, J P M Postma, W F van Gunsteren, A DiNola and J R Haak, "Molecular dynamics with coupling to an external bath", *J Chem Phys*, 1984, **81**, 3684–3690, DOI: 10.1063/1.448118.
- [249] P Langevin, "Sur la théorie du mouvement brownien", *C R Acad Sci*, 1908, **146**, 530–533.
- [250] D S Lemons and A Gythiel, "Paul Langevin's 1908 paper 'On the Theory of Brownian Motion' ['Sur la théorie du mouvement brownien,' C. R. Acad. Sci. (Paris) 146, 530–533 (1908)]", *Am J Phys*, 1997, **65**, 1079–1081, DOI: 10.1119/1.18725.
- [251] T Schneider and E Stoll, "Molecular-dynamics study of a three-dimensional one-component model for distortive phase transitions", *Phys Rev B*, 1978, **17**, 1302–1322, DOI: 10.1103/PhysRevB.17.1302.
- [252] A V Verkhovtsev, I A Solov'yov and A V Solov'yov, "Irradiation-driven molecular dynamics: a review", *Eur Phys J D*, 2021, **75**, 213, DOI: 10.1140/epjd/s10053-021-00223-3. 
- [253] I A Solov'yov, G B Sushko and A V Solov'yov, *MBN Explorer Users' Guide: Version 3.0*, MBN Research Center, Frankfurt am Main, Germany, 1st ed, 2017.
- [254] R Gaur, L Mishra, M A Siddiqi and B Atakan, "Ruthenium complexes as precursors for chemical vapor-deposition (CVD)", *RSC Adv*, 2014, **4**, 33785–33805, DOI: 10.1039/C4RA04701J. 
- [255] S Barth, M Huth and F Jungwirth, "Precursors for direct-write nanofabrication with electrons", *J Mater Chem C*, 2020, **8**, 15884–15919, DOI: 10.1039/D0TC03689G.
- [256] I Utke, P Swiderek, K Höflich, K Madajska, J Jurczyk, P Martinović and I Szymańska, "Coordination and organometallic precursors of group 10 and 11: Focused electron beam induced deposition of metals and insight gained from chemical vapour deposition, atomic layer deposition, and fundamental surface and gas phase studies", *Coord Chem Rev*, 2022, **458**, 213851, DOI: 10.1016/j.ccr.2021.213851. 

- [257] J-C Yu, M K Abdel-Rahman, D H Fairbrother and L McElwee-White, "Charged Particle-Induced Surface Reactions of Organometallic Complexes as a Guide to Precursor Design for Electron- and Ion-Induced Deposition of Nanostructures", *ACS Appl Mater Interfaces*, 2021, **13**, 48333–48348, DOI: 10.1021/acsami.1c12327.
- [258] B Luo and W L Gladfelter, "Chemical Vapor Deposition of Metals: W, Al, Cu and Ru", in *Chemical Vapour Deposition: Precursors, Processes and Applications*, The Royal Society of Chemistry, 2008, chap 7, pp 320–356, DOI: 10.1039/9781847558794-00320.
- [259] Q Wang, J G Ekerdt, D Gay, Y-M Sun and J M White, "Low-temperature chemical vapor deposition and scaling limit of ultrathin Ru films", *Appl Phys Lett*, 2004, **84**, 1380–1382, DOI: 10.1063/1.1650044.
- [260] U Banik, M T U Malik, S M S M Rahat and A K Mallik, "Performance enhancement of ruthenium-based supercapacitors: A review", *Energy Storage*, 2023, **5**, e380, DOI: 10.1002/est2.380.
- [261] D-S Yoon, J S Roh, H K Baik and S-M L and, "Future Direction for a Diffusion Barrier in Future High-Density Volatile and Nonvolatile Memory Devices", *Crit Rev Solid State Mater Sci*, 2002, **27**, 143–226, DOI: 10.1080/10408430208500495.
- [262] O Chyan, T N Arunagiri and T Ponnuswamy, "Electrodeposition of Copper Thin Film on Ruthenium : A Potential Diffusion Barrier for Cu Interconnects", *J Electrochem Soc*, 2003, **150**, C347, DOI: 10.1149/1.1565138.
- [263] R Chan, T N Arunagiri, Y Zhang, O Chyan, R M Wallace, M J Kim and T Q Hurd, "Diffusion Studies of Copper on Ruthenium Thin Film : A Plateable Copper Diffusion Barrier", *Electrochem Solid State Lett*, 2004, **7**, G154, DOI: 10.1149/1.1757113.
- [264] H Haick and D Cahen, "Making contact: Connecting molecules electrically to the macroscopic world", *Prog Surf Sci*, 2008, **83**, 217–261, DOI: 10.1016/j.progsurf.2008.04.002.
- [265] C R Brewer, O M Hawkins, N C Sheehan, J D Bullock, V D Kleiman, A V Walker and L McElwee-White, "Photochemistry of (η^3 -allyl)Ru(CO)₃X Precursors for Photoassisted Chemical Vapor Deposition", *Organometallics*, 2019, **38**, 4363–4370, DOI: 10.1021/acs.organomet.9b00628.
- [266] C R Brewer, N C Sheehan, J Herrera, A V Walker and L McElwee-White, "Photochemistry of (η^4 -diene)Ru(CO)₃ Complexes as Precursor Candidates for Photoassisted Chemical Vapor Deposition", *Organometallics*, 2022, **41**, 761–775, DOI: 10.1021/acs.organomet.1c00715.
- [267] O Jaenicke, R C Kerber, P Kirsch, E A K von Gustorf and R Rumin, "Quantum yields in photolysis of (diene)tricarbonyliron and bis(diene)carbonyliron complexes", *J Organomet Chem*, 1980, **187**, 361–373, DOI: 10.1016/S0022-328X(00)93429-6.
- [268] V Bachler, F-W Grevels, K Kerpen, G Olbrich and K Schaffner, "A Novel Facet of Carbonyliron-Diene Photochemistry: The η^4 -*s-trans* Isomer of the Classical Fe(CO)₃(η^4 -*s-cis*-1,3-butadiene) Discovered by Time-Resolved IR Spectroscopy and Theoretically Examined by Density Functional Methods", *Organometallics*, 2003, **22**, 1696–1711, DOI: 10.1021/om020785c.

- [269] T H Chang and J I Zink, "Photochemistry and single-crystal polarized absorption spectroscopy of (.eta.4-cyclooctatetraene)tricarbonyliron", *Inorg Chem*, 1985, **24**, 4016–4019, DOI: 10.1021/ic00218a011.
- [270] N Leadbeater, "Enlightening organometallic chemistry: the photochemistry of Fe(CO)₅ and the reaction chemistry of unsaturated iron carbonyl fragments", *Coord Chem Rev*, 1999, **188**, 35–70.
- [271] S A Trushin, W Fuss, K L Kompa and W E Schmid, "Femtosecond Dynamics of Fe(CO)₅ Photodissociation at 267 nm Studied by Transient Ionization", *J Phys Chem A*, 2000, **104**, 1997–2006, DOI: 10.1021/jp992474u.
- [272] J J Turner, M W George, M Poliakoff and R N Perutz, "Photochemistry of transition metal carbonyls", *Chem Soc Rev*, 2022, **51**, 5300–5329, DOI: 10.1039/D1CS00826A. 
- [273] L Bañares, T Baumert, M Bergt, B Kiefer and G Gerber, "The ultrafast photodissociation of Fe(CO)₅ in the gas phase", *J Chem Phys*, 1998, **108**, 5799–5811, DOI: 10.1063/1.475991.
- [274] B Andreides, A V Verkhovtsev, J Fedor and A V Solov'yov, "Role of the Molecular Environment in Quenching the Irradiation-Driven Fragmentation of Fe(CO)₅: A Reactive Molecular Dynamics Study", *J Phys Chem A*, 2023, **127**, 3757–3767, DOI: 10.1021/acs.jpca.2c08756. 
- [275] K Nagamori, M Haze, H Nakata, O Zingsheim, K Yamasaki and H Kohguchi, "Generation of Highly Vibrationally Excited CO in Sequential Photodissociation of Iron Carbonyl Complexes", *J Phys Chem A*, 2022, **126**, 306–313, DOI: 10.1021/acs.jpca.1c09922.
- [276] J Troß, J E Arias-Martinez, K Carter-Fenk, N C Cole-Filipiak, P Schrader, L M McCaslin, M Head-Gordon and K Ramasesha, "Femtosecond Core-Level Spectroscopy Reveals Involvement of Triplet States in the Gas-Phase Photodissociation of Fe(CO)₅", *J Am Chem Soc*, 2024, **146**, 22711–22723, DOI: 10.1021/jacs.4c07523.
- [277] Z-F Zhang and M-D Su, "The mechanistic investigations of photochemical decarbonylations and oxidative addition reactions for M(CO)₅ (M = Fe, Ru, Os) complexes", *RSC Adv*, 2019, **9**, 2626–2640, DOI: 10.1039/C8RA07669C. 
- [278] P L Bogdan and E Weitz, "A transient infrared spectroscopy study of coordinatively unsaturated ruthenium carbonyls", *J Am Chem Soc*, 1989, **111**, 3163–3167, DOI: 10.1021/ja00191a009.
- [279] J Li, G Schreckenbach and T Ziegler, "A Reassessment of the First Metal-Carbonyl Dissociation Energy in M(CO)₄ (M = Ni, Pd, Pt), M(CO)₅ (M = Fe, Ru, Os), and M(CO)₆ (M = Cr, Mo, W) by a Quasirelativistic Density Functional Method", *J Am Chem Soc*, 1995, **117**, 486–494, DOI: 10.1021/ja00106a056.
- [280] M Zlatar, M Allan and J Fedor, "Excited States of Pt(PF₃)₄ and Their Role in Focused Electron Beam Nanofabrication", *J Phys Chem C*, 2016, **120**, 10667–10674, DOI: 10.1021/acs.jpcc.6b02660.

- [281] **C P Souza**, A V Verkhovtsev, A V Walker, N J Mason, A V Solov'yov, L McElwee-White, M Zlatar and F Fantuzzi, "Excited-state dissociation of (η^4 -diene)Ru(CO)₃ precursors for photo-assisted chemical vapour deposition", *Phys Chem Chem Phys*, 2026, **28**, 17804–17817, DOI: 10.1039/d6cp00843g. 
- [282] P de Vera, A Verkhovtsev, G Sushko and A V Solov'yov, "Reactive molecular dynamics simulations of organometallic compound W(CO)₆ fragmentation", *Eur Phys J D*, 2019, **73**, 215, DOI: 10.1140/epjd/e2019-100232-9.
- [283] J-D Chai and M Head-Gordon, "Systematic optimization of long-range corrected hybrid density functionals", *J Chem Phys*, 2008, **128**, 084106, DOI: 10.1063/1.2834918.
- [284] M J Frisch, G W Trucks, H B Schlegel, G E Scuseria, M A Robb, J R Cheeseman, G Scalmani, V Barone, G A Petersson, H Nakatsuji, X Li, M Caricato, A V Marenich, J Bloino, B G Janesko, R Gomperts, B Mennucci, H P Hratchian, J V Ortiz, A F Izmaylov, J L Sonnenberg, D Williams-Young, F Ding, F Lipparini, F Egidi, J Goings, B Peng, A Petrone, T Henderson, D Ranasinghe, V G Zakrzewski, J Gao, N Rega, G Zheng, W Liang, M Hada, M Ehara, K Toyota, R Fukuda, J Hasegawa, M Ishida, T Nakajima, Y Honda, O Kitao, H Nakai, T Vreven, K Throssell, J A Montgomery Jr, J E Peralta, F Ogliaro, M J Bearpark, J J Heyd, E N Brothers, K N Kudin, V N Staroverov, T A Keith, R Kobayashi, J Normand, K Raghavachari, A P Rendell, J C Burant, S S Iyengar, J Tomasi, M Cossi, J M Millam, M Klene, C Adamo, R Cammi, J W Ochterski, R L Martin, K Morokuma, O Farkas, J B Foresman and D J Fox, *Gaussian 16 Revision A.03*, Gaussian Inc. Wallingford CT, 2016.
- [285] G Henkelman and H Jónsson, "Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points", *J Chem Phys*, 2000, **113**, 9978–9985, DOI: 10.1063/1.1323224.
- [286] F Neese, "Software update: The ORCA program system—Version 5.0", *WIREs Comput Mol Sci*,  2022, **12**, e1606, DOI: 10.1002/wcms.1606.
- [287] S Grimme, S Ehrlich and L Goerigk, "Effect of the damping function in dispersion corrected density functional theory", *J Comput Chem*, 2011, **32**, 1456–1465, DOI: 10.1002/jcc.21759.
- [288] F Weigend, "Accurate Coulomb-fitting basis sets for H to Rn", *Phys Chem Chem Phys*, 2006, **8**, 1057–1065, DOI: 10.1039/B515623H.
- [289] V Ásgeirsson, B O Birgisson, R Bjornsson, U Becker, F Neese, C Riplinger and H Jónsson, "Nudged Elastic Band Method for Molecular Reactions Using Energy-Weighted Springs Combined with Eigenvector Following", *J Chem Theory Comput*, 2021, **17**, 4929–4945, DOI: 10.1021/acs.jctc.1c00462.
- [290] R L Martin, "Natural transition orbitals", *J Chem Phys*, 2003, **118**, 4775–4777, DOI: 10.1063/1.1558471.
- [291] F Plasser and H Lischka, "Analysis of Excitonic and Charge Transfer Interactions from Quantum Chemical Calculations", *J Chem Theory Comput*, 2012, **8**, 2777–2789, DOI: 10.1021/ct300307c.
- [292] F Plasser, "TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations", *J Chem Phys*, 2020, **152**, 084108, DOI: 10.1063/1.5143076.

- [293] M P Mitoraj, A Michalak and T Ziegler, “A Combined Charge and Energy Decomposition Scheme for Bond Analysis”, *J Chem Theory Comput*, 2009, **5**, 962–975, DOI: 10.1021/ct800503d.
- [294] G te Velde, F M Bickelhaupt, E J Baerends, C Fonseca Guerra, S J A van Gisbergen, J G Snijders and T Ziegler, “Chemistry with ADF”, *J Comput Chem*, 2001, **22**, 931–967, DOI: 10.1002/jcc.1056.
- [295] E J Baerends, N F Aguirre, N D Austin, J Autschbach, F M Bickelhaupt, R Bulo, C Cappelli, A C T van Duin, F Egidi, C Fonseca Guerra, A Förster, M Franchini, T P M Goumans, T Heine, M Hellström, C R Jacob, L Jensen, M Krykunov, E van Lenthe, A Michalak, M M Mitoraj, J Neugebauer, V P Nicu, P Philipsen, H Ramanantoanina, R Rüger, G Schreckenbach, M Stener, M Swart, J M Thijssen, T Trnka, L Visscher, A Yakovlev and S van Gisbergen, “The Amsterdam Modeling Suite”, *J Chem Phys*, 2025, **162**, 162501, DOI: 10.1063/5.0258496.
- [296] C Adamo and V Barone, “Toward reliable density functional methods without adjustable parameters: The PBE0 model”, *J Chem Phys*, 1999, **110**, 6158–6170, DOI: 10.1063/1.478522.
- [297] E Van Lenthe and E J Baerends, “Optimized Slater-type basis sets for the elements 1–118”, *J Comput Chem*, 2003, **24**, 1142–1156, DOI: 10.1002/jcc.10255.
- [298] R Salzmann, C J Ziegler, N Godbout, M T McMahon, K S Suslick and E Oldfield, “Carbonyl Complexes of Iron(II), Ruthenium(II), and Osmium(II) 5,10,15,20-Tetraphenylporphyrinates: A Comparative Investigation by X-ray Crystallography, Solid-State NMR Spectroscopy, and Density Functional Theory”, *J Am Chem Soc*, 1998, **120**, 11323–11334, DOI: 10.1021/ja9740069.
- [299] M I Bruce, K Costuas, T Davin, B G Ellis, J-F Halet, C Lapinte, P J Low, M E Smith, B W Skelton, L Toupet and A H White, “Iron versus Ruthenium: Dramatic Changes in Electronic Structure Result from Replacement of One Fe by Ru in $[\{\text{Cp}^*(\text{dppe})\text{Fe}\}\text{-CC-CC-}\{\text{Fe}(\text{dppe})\text{Cp}^*\}]^{n+}$ ($n = 0, 1, 2$)”, *Organometallics*, 2005, **24**, 3864–3881, DOI: 10.1021/om050293a.
- [300] S Gückel, J B G Gluyas, S El-Tarhuni, A N Sobolev, M W Whiteley, J-F Halet, C Lapinte, M Kaupp and P J Low, “Iron versus Ruthenium: Clarifying the Electronic Differences between Prototypical Mixed-Valence Organometallic Butadiynediyl Bridged Molecular Wires”, *Organometallics*, 2018, **37**, 1432–1445, DOI: 10.1021/acs.organomet.8b00099.
- [301] B Dickens and W N Lipscomb, “Molecular and Valence Structures of Complexes of Cyclo-Octatetraene with Iron Tricarbonyl”, *J Chem Phys*, 1962, **37**, 2084–2093, DOI: 10.1063/1.1733429.
- [302] M A Bennett, H Neumann, A C Willis, V Ballantini, P Pertici and B E Mann, “Synthesis, Structure, and Fluxional Behavior of Bis(cyclooctatetraene)ruthenium(0) and Its Derivatives”, *Organometallics*, 1997, **16**, 2868–2878, DOI: 10.1021/om970065j.
- [303] E R Davidson, K L Kunze, F B C Machado and S J Chakravorty, “The transition metal–carbonyl bond”, *Acc Chem Res*, 1993, **26**, 628–635, DOI: 10.1021/ar00036a004.

- [304] G Frenking, I Fernández, N Holzmann, S Pan, I Krossing and M Zhou, “Metal–CO Bonding in Mononuclear Transition Metal Carbonyl Complexes”, *JACS Au*, 2021, **1**, 623–645, DOI: 10.1021/jacsau.1c00106. 
- [305] A Krapp, K K Pandey and G Frenking, “Transition Metal–Carbon Complexes. A Theoretical Study”, *J Am Chem Soc*, 2007, **129**, 7596–7610, DOI: 10.1021/ja0691324.
- [306] W Kennedy, V Pattathil, Y Wei, F Fantuzzi and C Prancevicius, “Ambient Temperature Isolation of a Monatomic Boron(0) Complex”, *J Am Chem Soc*, 2025, **147**, 3500–3506, DOI: 10.1021/jacs.4c14915.
- [307] G Ganguly, S Pathak and A Paul, “Unraveling the stability of cyclobutadiene complexes using aromaticity markers”, *Phys Chem Chem Phys*, 2021, **23**, 16005–16012, DOI: 10.1039/D1CP01467F.
- [308] P B Karadakov, “Ground- and Excited-State Aromaticity and Antiaromaticity in Benzene and Cyclobutadiene”, *J Phys Chem A*, 2008, **112**, 7303–7309, DOI: 10.1021/jp8037335.
- [309] F Fantuzzi, T M Cardozo and M A C Nascimento, “The Nature of the Singlet and Triplet States of Cyclobutadiene as Revealed by Quantum Interference”, *ChemPhysChem*, 2016, **17**, 288–295, DOI: 10.1002/cphc.201500885.
- [310] D Jacquemin, E A Perpète, I Ciofini and C Adamo, “Assessment of the ω B97 family for excited-state calculations”, *Theor Chem Acc*, 2011, **128**, 127–136, DOI: 10.1007/s00214-010-0783-x.
- [311] A J Atkins, F Talotta, L Freitag, M Boggio-Pasqua and L González, “Assessing Excited State Energy Gaps with Time-Dependent Density Functional Theory on Ru(II) Complexes”, *J Chem Theory Comput*, 2017, **13**, 4123–4145, DOI: 10.1021/acs.jctc.7b00379.
- [312] A D Laurent and D Jacquemin, “TD-DFT benchmarks: A review”, *Int J Quantum Chem*, 2013, **113**, 2019–2039, DOI: 10.1002/qua.24438. 
- [313] A Vlček and S Zálšíš, “Modeling of charge-transfer transitions and excited states in d^6 transition metal complexes by DFT techniques”, *Coord Chem Rev*, 2007, **251**, A Special Issue Highlighting the Many Aspects of the Electronic Spectroscopy of Inorganic Compounds, 258–287, DOI: 10.1016/j.ccr.2006.05.021.
- [314] J S Sears, T Koerzdoerfer, C-R Zhang and J-L Brédas, “Communication: Orbital instabilities and triplet states from time-dependent density functional theory and long-range corrected functionals”, *J Chem Phys*, 2011, **135**, 151103, DOI: 10.1063/1.3656734. 
- [315] N T Maitra, F Zhang, R J Cave and K Burke, “Double excitations within time-dependent density functional theory linear response”, *J Chem Phys*, 2004, **120**, 5932–5937, DOI: 10.1063/1.1651060.
- [316] P Elliott, S Goldson, C Canahui and N T Maitra, “Perspectives on double-excitations in TDDFT”, *Chem Phys*, 2011, **391**, Open problems and new solutions in time dependent density functional theory, 110–119, DOI: 10.1016/j.chemphys.2011.03.020.
- [317] Y Yang, E R Davidson and W Yang, “Nature of ground and electronic excited states of higher acenes”, *Proc Natl Acad Sci USA*, 2016, **113**, E5098–E5107, DOI: 10.1073/pnas.1606021113. 

- [318] J H Starcke, M Wormit, J Schirmer and A Dreuw, “How much double excitation character do the lowest excited states of linear polyenes have?”, *Chem Phys*, 2006, **329**, Electron Correlation and Multimode Dynamics in Molecules, 39–49, DOI: 10.1016/j.chemphys.2006.07.020.
- [319] M T do Casal, J M Toldo, M Barbatti and F Plasser, “Classification of doubly excited molecular electronic states”, *Chem Sci*, 2023, **14**, 4012–4026, DOI: 10.1039/D2SC06990C.
- [320] B G Levine, C Ko, J Quenneville and T J Martínez, “Conical intersections and double excitations in time-dependent density functional theory”, *Mol Phys*, 2006, **104**, 1039–1051, DOI: 10.1080/00268970500417762.
- [321] L González, D Escudero and L Serrano-Andrés, “Progress and Challenges in the Calculation of Electronic Excited States”, *ChemPhysChem*, 2012, **13**, 28–51, DOI: 10.1002/cphc.201100200.
- [322] W C Bigelow, D L Pickett and W A Zisman, “Oleophobic monolayers: I. Films adsorbed from solution in non-polar liquids”, *J Colloid Sci*, 1946, **1**, 513–538, DOI: 10.1016/0095-8522(46)90059-1.
- [323] V M Mirsky, “New electroanalytical applications of self-assembled monolayers”, *Trends Anal Chem*, 2002, **21**, 439–450, DOI: 10.1016/S0165-9936(02)00601-5.
- [324] D Mandler and S Kraus-Ophir, “Self-assembled monolayers (SAMs) for electrochemical sensing”, *J Solid State Electrochem*, 2011, **15**, 1535–1558, DOI: 10.1007/s10008-011-1493-6.
- [325] N K Chaki and K Vijayamohanan, “Self-assembled monolayers as a tunable platform for biosensor applications”, *Biosens Bioelectron*, 2002, **17**, 1–12, DOI: 10.1016/S0956-5663(01)00277-9.
- [326] S K Arya, P R Solanki, M Datta and B D Malhotra, “Recent advances in self-assembled monolayers based biomolecular electronic devices”, *Biosens Bioelectron*, 2009, **24**, 2810–2817, DOI: 10.1016/j.bios.2009.02.008.
- [327] J H Schön, H Meng and Z Bao, “Self-assembled monolayer organic field-effect transistors”, *Nature*, 2001, **413**, 713–716, DOI: 10.1038/35099520.
- [328] M Halik and A Hirsch, “The Potential of Molecular Self-Assembled Monolayers in Organic Electronic Devices”, *Adv Mater*, 2011, **23**, 2689–2695, DOI: 10.1002/adma.201100337.
- [329] S Casalini, C A Bortolotti, F Leonardi and F Biscarini, “Self-assembled monolayers in organic electronics”, *Chem Soc Rev*, 2017, **46**, 40–71, DOI: 10.1039/C6CS00509H.
- [330] M Singh, N Kaur and E Comini, “The role of self-assembled monolayers in electronic devices”, *J Mater Chem C*, 2020, **8**, 3938–3955, DOI: 10.1039/D0TC00388C.
- [331] S T Marshall, M O’Brien, B Oetter, A Corpuz, R M Richards, D K Schwartz and J W Medlin, “Controlled selectivity for palladium catalysts using self-assembled monolayers”, *Nat Mater*, 2010, **9**, 853–858, DOI: 10.1038/nmat2849.
- [332] C A Schoenbaum, D K Schwartz and J W Medlin, “Controlling the Surface Environment of Heterogeneous Catalysts Using Self-Assembled Monolayers”, *Acc Chem Res*, 2014, **47**, 1438–1445, DOI: 10.1021/ar500029y.
- [333] J Aizenberg, A J Black and G M Whitesides, “Control of crystal nucleation by patterned self-assembled monolayers”, *Nature*, 1999, **398**, 495–498, DOI: 10.1038/19047.

- [334] A Kumar, H A Biebuyck and G M Whitesides, "Patterning Self-Assembled Monolayers: Applications in Materials Science", *Langmuir*, 1994, **10**, 1498–1511, DOI: 10.1021/1a00017a030.
- [335] N K Chaki, M Aslam, J Sharma and K Vijayamohanan, "Applications of self-assembled monolayers in materials chemistry", *J Chem Sci*, 2001, **113**, 659–670, DOI: 10.1007/BF02708798.
- [336] J C Love, L A Estroff, J K Kriebel, R G Nuzzo and G M Whitesides, "Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology", *Chem Rev*, 2005, **105**, 1103–1170, DOI: 10.1021/cr0300789.
- [337] C Vericat, M E Vela, G Benitez, P Carro and R C Salvarezza, "Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system", *Chem Soc Rev*, 2010, **39**, 1805–1834, DOI: 10.1039/B907301A.
- [338] R G Nuzzo and D L Allara, "Adsorption of bifunctional organic disulfides on gold surfaces", *J Am Chem Soc*, 1983, **105**, 4481–4483, DOI: 10.1021/ja00351a063.
- [339] Z Shi, P Lu and A V Walker, "UV Photoactivated Room Temperature CVD of Aluminum on Functionalized Self-Assembled Monolayers Adsorbed on Au", *Langmuir*, 2012, **28**, 16909–16916, DOI: 10.1021/la303454d.
- [340] L Kankate, A Turchanin and A Götzhäuser, "On the Release of Hydrogen from the S–H groups in the Formation of Self-Assembled Monolayers of Thiols", *Langmuir*, 2009, **25**, 10435–10438, DOI: 10.1021/la902168u.
- [341] F Tielens and E Santos, "AuS and SH Bond Formation/Breaking during the Formation of Alkanethiol SAMs on Au(111): A Theoretical Study", *J Phys Chem C*, 2010, **114**, 9444–9452, DOI: 10.1021/jp102036r.
- [342] L Zhang, W A Goddard III and S Jiang, "Molecular Simulation study of the c(4×2) superlattice structure of alkanethiol self-assembled monolayers on Au(111)", *J Chem Phys*, 2002, **117**, 7342–7349, DOI: 10.1063/1.1507777.
- [343] A Ulman, "Formation and Structure of Self-Assembled Monolayers", *Chem Rev*, 1996, **96**, 1533–1554, DOI: 10.1021/cr9502357.
- [344] P Fenter, A Eberhardt, K S Liang and P Eisenberger, "Epitaxy and chainlength dependent strain in self-assembled monolayers", *J Chem Phys*, 1997, **106**, 1600–1608, DOI: 10.1063/1.473281.
- [345] J Hautman and M L Klein, "Molecular dynamics simulation of the effects of temperature on a dense monolayer of long-chain molecules", *J Chem Phys*, 1990, **93**, 7483–7492, DOI: 10.1063/1.459423.
- [346] C D Bain, E B Troughton, Y T Tao, J Evall, G M Whitesides and R G Nuzzo, "Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold", *J Am Chem Soc*, 1989, **111**, 321–335, DOI: 10.1021/ja00183a049.
- [347] H Gojzewski, M Kappl and A Ptak, "Effect of the Chain Length and Temperature on the Adhesive Properties of Alkanethiol Self-Assembled Monolayers", *Langmuir*, 2017, **33**, 11862–11868, DOI: 10.1021/acs.langmuir.7b01921.

- [348] R Desikan, S Armel, H M Meyer and T Thundat, "Effect of chain length on nanomechanics of alkanethiol self-assembly", *Nanotechnology*, 2007, **18**, 424028, DOI: 10.1088/0957-4484/18/42/424028.
- [349] M D Malinsky, K L Kelly, G C Schatz and R P Van Duyne, "Chain Length Dependence and Sensing Capabilities of the Localized Surface Plasmon Resonance of Silver Nanoparticles Chemically Modified with Alkanethiol Self-Assembled Monolayers", *J Am Chem Soc*, 2001, **123**, 1471–1482, DOI: 10.1021/ja003312a.
- [350] B Wang, J Luo, X Wang, H Wang and J G Hou, "Dielectric Properties and Frequency Response of Self-Assembled Monolayers of Alkanethiols", *Langmuir*, 2004, **20**, 5007–5012, DOI: 10.1021/la036295m.
- [351] F Schreiber, "Structure and growth of self-assembling monolayers", *Prog Surf Sci*, 2000, **65**, 151–257, DOI: 10.1016/S0079-6816(00)00024-1.
- [352] R G Nuzzo, L H Dubois and D L Allara, "Fundamental studies of microscopic wetting on organic surfaces. 1. Formation and structural characterization of a self-consistent series of polyfunctional organic monolayers", *J Am Chem Soc*, 1990, **112**, 558–569, DOI: 10.1021/ja00158a012.
- [353] G E Poirier, M J Tarlov and H E Rushmeier, "Two-Dimensional Liquid Phase and the px.sqroot.3 Phase of Alkanethiol Self-Assembled Monolayers on Au(111)", *Langmuir*, 1994, **10**, 3383–3386, DOI: 10.1021/la00022a004.
- [354] H Sellers, A Ulman, Y Shnidman and J E Eilers, "Structure and binding of alkanethiolates on gold and silver surfaces: implications for self-assembled monolayers", *J Am Chem Soc*, 1993, **115**, 9389–9401, DOI: 10.1021/ja00074a004.
- [355] L Strong and G M Whitesides, "Structures of self-assembled monolayer films of organosulfur compounds adsorbed on gold single crystals: electron diffraction studies", *Langmuir*, 1988, **4**, 546–558, DOI: 10.1021/la00081a009.
- [356] N Camillone III, C E D Chidsey, G Liu and G Scoles, "Substrate dependence of the surface structure and chain packing of docosyl mercaptan self-assembled on the (111), (110), and (100) faces of single crystal gold", *J Chem Phys*, 1993, **98**, 4234–4245, DOI: 10.1063/1.465030.
- [357] L H Dubois, B R Zegarski and R G Nuzzo, "Molecular ordering of organosulfur compounds on Au(111) and Au(100): Adsorption from solution and in ultrahigh vacuum", *J Chem Phys*, 1993, **98**, 678–688, DOI: 10.1063/1.464613.
- [358] P Maksymovych, D C Sorescu and J T Yates, "Methanethiolate Adsorption Site on Au(111): A Combined STM/DFT Study at the Single-Molecule Level", *J Phys Chem B*, 2006, **110**, 21161–21167, DOI: 10.1021/jp0625964.
- [359] T T Järvi, A C T van Duin, K Nordlund and W A Goddard III, "Development of Interatomic ReaxFF Potentials for Au–S–C–H Systems", *J Phys Chem A*, 2011, **115**, 10315–10322, DOI: 10.1021/jp201496x.

- [360] Y Ahn, J K Saha, G C Schatz and J Jang, “Molecular Dynamics Study of the Formation of a Self-Assembled Monolayer on Gold”, *J Phys Chem C*, 2011, **115**, 10668–10674, DOI: 10.1021/jp200447k.
- [361] H Häkkinen, “The gold–sulfur interface at the nanoscale”, *Nat Chem*, 2012, **4**, 443–455, DOI: 10.1038/nchem.1352.
- [362] D Stefanakis, V Harmandaris, G Kopidakis and I Remediakis, “From Order to Disorder of Alkanethiol Self-Assembled Monolayers on Complex Au (211), (221), and (311) Surfaces: Impact of the Substrate”, *J Phys Chem C*, 2021, **125**, 3495–3508, DOI: 10.1021/acs.jpcc.0c08328.
- [363] K Haume, N J Mason and A V Solov'yov, “Modeling of nanoparticle coatings for medical applications”, *Eur Phys J D*, 2016, **70**, 181, DOI: 10.1140/epjd/e2016-70282-6. 
- [364] T Djebaili, S Abel, M Marchi and J Richardi, “Influence of Force-Field Parameters on the Atomistic Simulations of Metallic Surfaces and Nanoparticles”, *J Phys Chem C*, 2017, **121**, 27758–27765, DOI: 10.1021/acs.jpcc.7b09857.
- [365] T-W Li, I Chao and Y-T Tao, “Relationship between Packing Structure and Headgroups of Self-Assembled Monolayers on Au(111): Bridging Experimental Observations through Computer Simulations”, *J Phys Chem B*, 1998, **102**, 2935–2946, DOI: 10.1021/jp980049f.
- [366] R Bhatia and B J Garrison, “Structure of c(4×2) Superlattice in Alkanethiolate Self-Assembled Monolayers”, *Langmuir*, 1997, **13**, 4038–4043, DOI: 10.1021/la962055d.
- [367] J J Gerdy and W A Goodard, “Atomistic Structure for Self-Assembled Monolayers of Alkanethiols on Au(111) Surfaces”, *J Am Chem Soc*, 1996, **118**, 3233–3236, DOI: 10.1021/ja951784x.
- [368] A K Rappe, C J Casewit, K S Colwell, W A Goddard III and W M Skiff, “UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations”, *J Am Chem Soc*, 1992, **114**, 10024–10035, DOI: 10.1021/ja00051a040.
- [369] W L Jorgensen, D S Maxwell and J Tirado-Rives, “Development and testing of the OPLS All-Atom Force Field on conformational energetics and properties of organic liquids”, *J Am Chem Soc*, 1996, **118**, 11225–11236, DOI: 10.1021/ja9621760.
- [370] L S Dodda, I Cabeza de Vaca, J Tirado-Rives and W L Jorgensen, “LigParGen web server: An automatic OPLS-AA parameter generator for organic ligands”, *Nucleic Acids Res*, 2017, **45**, W331–W336, DOI: 10.1093/nar/gkx312. 
- [371] P Bhadra and S W I Siu, “Comparison of biomolecular force fields for alkanethiol self-assembled monolayer simulations”, *J Phys Chem C*, 2017, **121**, 26340–26349, DOI: 10.1021/acs.jpcc.7b08092.
- [372] Y Zhao and D G Truhlar, “The Mo6 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four Mo6-class functionals and 12 other functionals”, *Theor Chem Acc*, 2008, **120**, 215–241, DOI: 10.1007/s00214-007-0310-x. 

- [373] E D Glendenning, C R Landis and F Weinhold, “Natural bond orbital methods”, *WIREs Comput Mol Sci*, 2012, **2**, 1–42, DOI: 10.1002/wcms.51.
- [374] G B Sushko, I A Solov'yov and A V Solov'yov, “Modeling MesoBioNano systems with MBN Studio made easy”, *J Mol Graph Model*, 2019, **88**, 247–260, DOI: 10.1016/j.jmgm.2019.02.003.
- [375] M W Finnis and J E Sinclair, “A simple empirical N-body potential for transition metals”, *Philos Mag*, 1984, **50**, 45–55, DOI: 10.1080/01418618408244210.
- [376] G J Ackland and R Thetford, “An improved N-body semi-empirical model for body-centred cubic transition metals”, *Philos Mag*, 1987, **56**, 15–30, DOI: 10.1080/01418618708204464.
- [377] P K Ghorai and S C Glotzer, “Molecular Dynamics Simulation Study of Self-Assembled Monolayers of Alkanethiol Surfactants on Spherical Gold Nanoparticles”, *J Phys Chem C*, 2007, **111**, 15857–15862, DOI: 10.1021/jp0746289.
- [378] B Quentrec and C Brot, “New method for searching for neighbors in molecular dynamics computations”, *J Comput Phys*, 1973, **13**, 430–432, DOI: 10.1016/0021-9991(73)90046-6.
- [379] R T McGibbon, K A Beauchamp, M P Harrigan, C Klein, J M Swails, C X Hernández, C R Schwantes, L-P Wang, T J Lane and V S Pande, “MDTraj: A Modern Open Library for the Analysis of Molecular Dynamics Trajectories”, *Biophys J*, 2015, **109**, 1528–1532, DOI: 10.1016/j.bpj.2015.08.015.
- [380] J D Hunter, “Matplotlib: A 2D graphics environment”, *Comput Sci Eng*, 2007, **9**, 90–95, DOI: 10.1109/MCSE.2007.55.
- [381] R Pool, P Schapotschnikow and T J H Vlugt, “Solvent Effects in the Adsorption of Alkyl Thiols on Gold Structures: A Molecular Simulation Study”, *J Phys Chem C*, 2007, **111**, 10201–10212, DOI: 10.1021/jp071491d.
- [382] I Leontyev and A Stuchebrukhov, “Accounting for electronic polarization in non-polarizable force fields”, *Phys Chem Chem Phys*, 2011, **13**, 2613–2626, DOI: 10.1039/c0cp01971b.
- [383] L H Dubois and R G Nuzzo, “Synthesis, Structure, and Properties of Model Organic Surfaces”, *Annu Rev Phys Chem*, 1992, **43**, 437–463, DOI: 10.1146/annurev.pc.43.100192.002253.
- [384] T Liang, T-R Shan, Y-T Cheng, B D Devine, M Noordhoek, Y Li, Z Lu, S R Phillpot and S B Sinnott, “Classical atomistic simulations of surfaces and heterogeneous interfaces with the charge-optimized many body (COMB) potentials”, *Mater Sci Eng R Reports*, 2013, **74**, 255–279, DOI: 10.1016/j.mser.2013.07.001.
- [385] A Thompson, L Swiler, C Trott, S Foiles and G Tucker, “Spectral neighbor analysis method for automated generation of quantum-accurate interatomic potentials”, *J Comput Phys*, 2015, **285**, 316–330, DOI: 10.1016/j.jcp.2014.12.018.
- [386] H Wang, L Zhang, J Han and W E, “DeePMD-kit: A deep learning package for many-body potential energy representation and molecular dynamics”, *Comput Phys Commun*, 2018, **228**, 178–184, DOI: 10.1016/j.cpc.2018.03.016.

- [387] C A McCandler, A Pihlajamäki, S Malola, H Häkkinen and K A Persson, “Gold–thiolate nanocluster dynamics and intercluster reactions enabled by a machine learned interatomic potential”, *ACS Nano*, 2024, **18**, 19014–19023, DOI: 10.1021/acsnano.4c03094. 
- [388] Y Wang, D S N D Samarasinghe, H Deng, B Liu and C M Aikens, “Gaussian process approach to constructing transferable force fields for thiolate-protected gold nanoclusters”, *J Chem Inf Model*, 2025, **65**, 3892–3902, DOI: 10.1021/acs.jcim.4c01495.
- [389] N Boens, V Leen and W Dehaen, “Fluorescent indicators based on BODIPY”, *Chem Soc Rev*, 2012, **41**, 1130–1172, DOI: 10.1039/C1CS15132K.
- [390] A Loudet and K Burgess, “BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties”, *Chem Rev*, 2007, **107**, 4891–4932, DOI: 10.1021/cr078381n.
- [391] A Kamkaew, S H Lim, H B Lee, L V Kiew, L Y Chung and K Burgess, “BODIPY dyes in photodynamic therapy”, *Chem Soc Rev*, 2013, **42**, 77–88, DOI: 10.1039/C2CS35216H.
- [392] A Turksoy, D Yildiz and E U Akkaya, “Photosensitization and controlled photosensitization with BODIPY dyes”, *Coord Chem Rev*, 2019, **379**, Novel and Smart Photosensitizers from Molecule to Nanoparticle, 47–64, DOI: 10.1016/j.ccr.2017.09.029.
- [393] P Lu, K-Y Chung, A Stafford, M Kiker, K Kafle and Z A Page, “Boron dipyrromethene (BODIPY) in polymer chemistry”, *Polym Chem*, 2021, **12**, 327–348, DOI: 10.1039/D0PY01513J.
- [394] L J Patalag, S Ahadi, O Lashchuk, P G Jones, S Ebbinghaus and D B Werz, “GlycoBODIPYs: Sugars Serving as a Natural Stock for Water-soluble Fluorescent Probes of Complex Chiral Morphology”, *Angew Chem Int Ed*, 2021, **60**, 8766–8771, DOI: 10.1002/anie.202016764. 
- [395] P Kaur and K Singh, “Recent advances in the application of BODIPY in bioimaging and chemosensing”, *J Mater Chem C*, 2019, **7**, 11361–11405, DOI: 10.1039/C9TC03719E.
- [396] A C Scanone, S C Santamarina, D A Heredia, E N Durantini and A M Durantini, “Functionalized Magnetic Nanoparticles with BODIPYs for Bioimaging and Antimicrobial Therapy Applications”, *ACS Appl Bio Mater*, 2020, **3**, 1061–1070, DOI: 10.1021/acsbm.9b01035.
- [397] T Zhang, C Ma, T Sun and Z Xie, “Unadulterated BODIPY nanoparticles for biomedical applications”, *Coord Chem Rev*, 2019, **390**, 76–85, DOI: 10.1016/j.ccr.2019.04.001.
- [398] L Yuan, W Lin, K Zheng, L He and W Huang, “Far-red to near infrared analyte-responsive fluorescent probes based on organic fluorophore platforms for fluorescence imaging”, *Chem Soc Rev*, 2013, **42**, 622–661, DOI: 10.1039/C2CS35313J.
- [399] Y Ni and J Wu, “Far-red and near infrared BODIPY dyes: synthesis and applications for fluorescent pH probes and bio-imaging”, *Org Biomol Chem*, 2014, **12**, 3774–3791, DOI: 10.1039/C3OB42554A.
- [400] Y Zhang, K-H Song, S Tang, L Ravelo, J Cusido, C Sun, H F Zhang and F M Raymo, “Far-Red Photoactivatable BODIPYs for the Super-Resolution Imaging of Live Cells”, *J Am Chem Soc*, 2018, **140**, 12741–12745, DOI: 10.1021/jacs.8b09099.

- [401] J Bañuelos, “BODIPY Dye, the Most Versatile Fluorophore Ever?”, *Chem Rec*, 2016, **16**, 335–348, DOI: 10.1002/tcr.201500238.
- [402] L Bonardi, G Ulrich and R Ziessel, “Tailoring the Properties of Boron–Dipyrromethene Dyes with Acetylenic Functions at the 2,6,8 and 4-B Substitution Positions”, *Org Lett*, 2008, **10**, 2183–2186, DOI: 10.1021/o1800560b.
- [403] A Prieto-Castañeda, E Avellanal-Zaballa, L Gartzia-Rivero, L Cerdán, A R Agarrabeitia, I García-Moreno, J Bañuelos and M J Ortiz, “Tailoring the Molecular Skeleton of Aza-BODIPYs to Design Photostable Red-Light-Emitting Laser Dyes”, *ChemPhotoChem*, 2019, **3**, 75–85, DOI: 10.1002/cptc.201800225.
- [404] R Mamgain and F V Singh, “Selenium-Based Fluorescence Probes for the Detection of Bioactive Molecules”, *ACS Org Inorg Au*, 2022, **2**, 262–288, DOI: 10.1021/acsoiginorgau.1c00047. 
- [405] J Fernández-Lodeiro, M F Pinatto-Botelho, A A Soares-Paulino, A C Gonçalves, B A Sousa, C Princival and A A Dos Santos, “Synthesis and biological properties of selenium- and tellurium-containing dyes”, *Dyes Pigm*, 2014, **110**, 1st International Caparica Conference on Chromogenic and Emissive Materials, 28–48, DOI: 10.1016/j.dyepig.2014.04.044.
- [406] S T Manjare, Y Kim and D G Churchill, “Selenium- and Tellurium-Containing Fluorescent Molecular Probes for the Detection of Biologically Important Analytes”, *Acc Chem Res*, 2014, **47**, 2985–2998, DOI: 10.1021/ar500187v.
- [407] Í A O Bozzi, L A Machado, E B T Diogo, F G Delolo, L O F Barros, G A P Graça, M H Araujo, F T Martins, L F Pedrosa, L C da Luz, E S Moraes, F S Rodembusch, J S F Guimarães, A G Oliveira, S H Röttger, D B Werz, **C P Souza**, F Fantuzzi, J Han, T B Marder, H Braunschweig and E N da Silva Júnior, “Electrochemical Diselenation of BODIPY Fluorophores for Bioimaging Applications and Sensitization of $^1\text{O}_2$ ”, *Chem Eur J*, 2024, **30**, e202303883, DOI: 10.1002/chem.202303883.
- [408] T H Dunning, “Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen”, *J Chem Phys*, 1989, **90**, 1007–1023, DOI: 10.1063/1.456153.
- [409] A K Wilson, D E Woon, K A Peterson and T H Dunning, “Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton”, *J Chem Phys*, 1999, **110**, 7667–7676, DOI: 10.1063/1.478678.
- [410] D M York and M Karplus, “A Smooth Solvation Potential Based on the Conductor-Like Screening Model”, *J Phys Chem A*, 1999, **103**, 11060–11079, DOI: 10.1021/jp9920971.
- [411] B Le Guennic and D Jacquemin, “Taking Up the Cyanine Challenge with Quantum Tools”, *Acc Chem Res*, 2015, **48**, 530–537, DOI: 10.1021/ar500447q. 
- [412] I Sandler, J Chen, M Taylor, S Sharma and J Ho, “Accuracy of DLPNO-CCSD(T): Effect of Basis Set and System Size”, *J Phys Chem A*, 2021, **125**, 1553–1563, DOI: 10.1021/acs.jpca.0c11270.

- [413] E Akhuseyin Yildiz, E Yabaş, F Sözmen, Y Bozkurt, A Karatay, B Boyacioglu, H Ünver and A Elmali, “Effects of Heavy Iodine Atoms and π -Expanded Conjugation on Charge Transfer Dynamics in Carboxylic Acid BODIPY Derivatives as Triplet Photosensitizers”, *ChemPhysChem*, 2023, **24**, e202200735, DOI: 10.1002/cphc.202200735.
- [414] B A McGuire, “2018 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules”, *Astrophys J Suppl Ser*, 2018, **239**, 17, DOI: 10.3847/1538-4365/aae5d2. 
- [415] B A McGuire, “2021 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules”, *Astrophys J Suppl Ser*, 2022, **259**, 30, DOI: 10.3847/1538-4365/ac2a48. 
- [416] A A Boogert, P A Gerakines and D C Whittet, “Observations of the Icy Universe”, *Annu Rev Astron Astrophys*, 2015, **53**, 541–581, DOI: 10.1146/annurev-astro-082214-122348.
- [417] M K McClure, W R M Rocha, K M Pontoppidan, N Crouzet, L E U Chu, E Dartois, T Lamberts, J A Noble, Y J Pendleton, G Perotti, D Qasim, M G Rachid, Z L Smith, F Sun, T L Beck, A C A Boogert, W A Brown, P Caselli, S B Charnley, H M Cuppen, H Dickinson, M N Drozdovskaya, E Egami, J Erkal, H Fraser, R T Garrod, D Harsono, S Ioppolo, I Jiménez-Serra, M Jin, J K Jørgensen, L E Kristensen, D C Lis, M R S McCoustra, B A McGuire, G J Melnick, K I Öberg, M E Palumbo, T Shimonishi, J A Sturm, E F van Dishoeck and H Linnartz, “An Ice Age JWST inventory of dense molecular cloud ices”, *Nat Astron*, 2023, **7**, 431–443, DOI: 10.1038/s41550-022-01875-w.
- [418] W R M Rocha, E F van Dishoeck, M E Ressler, M L van Gelder, K Slavicinska, N G C Brunken, H Linnartz, T P Ray, H Beuther, A Caratti o Garatti, V Geers, P J Kavanagh, P D Klaassen, K Justtanont, Y Chen, L Francis, C Gieser, G Perotti, Ł Tychoniec, M Barsony, L Majumdar, V J M le Gouellec, L E U Chu, B W P Lew, T Henning and G Wright, “JWST Observations of Young protoStars (JOYS+): Detecting icy complex organic molecules and ions”, *A&A*, 2024, **683**, DOI: 10.1051/0004-6361/202348427. 
- [419] J A Noble, H J Fraser, Z L Smith, E Dartois, A C A Boogert, H M Cuppen, H J Dickinson, F Dulieu, E Egami, J Erkal, B M Giuliano, B Husquinet, T Lamberts, B Maté, M K McClure, M E Palumbo, T Shimonishi, F Sun, J B Bergner, W A Brown, P Caselli, E Congiu, M N Drozdovskaya, V J Herrero, S Ioppolo, I Jimenez-Serra, H Linnartz, G J Melnick, B A McGuire, K I Oberg, G Perotti, D Qasim, W R M Rocha and R G Urso, “Detection of the elusive dangling OH ice features at $\sim 2.7 \mu\text{m}$ in Chamaeleon I with JWST NIRCam”, *Nat Astron*, 2024, **8**, 1169–1180, DOI: 10.1038/s41550-024-02307-7.
- [420] N G C Brunken, W R M Rocha, E F van Dishoeck, R Gutermuth, H Tyagi, K Slavicinska, P Nazari, S T Megeath, N J Evans II, M Narang, P Manoj, A E Rubinstein, D M Watson, L W Looney, H Linnartz, A Caratti o Garatti, H Beuther, H Linz, P Klaassen, C A Poteet, S Federman, G Anglada, P Atnagulov, T L Bourke, W J Fischer, E Furlan, J Green, N Habel, L Hartmann, N Karnath, M Osorio, J Muzerolle Page, R Pokhrel, R Rahatgaonkar, P Sheehan, T Stanke, A M Stutz, J J Tobin, Ł Tychoniec, S Wolk and Y-L Yang, “JWST observations of $^{13}\text{CO}_2$ ice”, *A&A*, 2024, **685**, DOI: 10.1051/0004-6361/202348718. 

- [421] M M Hedman, M S Tiscareno, M R Showalter, L N Fletcher, O R T King, J Harkett, M T Roman, N Rowe-Gurney, H B Hammel, S N Milam, M El Moutamid, R J Cartwright, I de Pater and E M Molter, “Water-Ice Dominated Spectra of Saturn’s Rings and Small Moons From JWST”, *J Geophys Res Planets*, 2024, **129**, e2023JE008236, DOI: 10.1029/2023JE008236. 
- [422] G L Villanueva, H B Hammel, S N Milam, S Faggi, V Kofman, L Roth, K P Hand, L Paganini, J Stansberry, J Spencer, S Protopapa, G Strazzulla, G Cruz-Mermy, C R Glein, R Cartwright and G Liuzzi, “Endogenous CO₂ ice mixture on the surface of Europa and no detection of plume activity”, *Science*, 2023, **381**, 1305–1308, DOI: 10.1126/science.adg4270. 
- [423] S K Trumbo and M E Brown, “The distribution of CO₂ on Europa indicates an internal source of carbon”, *Science*, 2023, **381**, 1308–1311, DOI: 10.1126/science.adg4155.
- [424] K I Öberg, “Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules”, *Chem Rev*, 2016, **116**, 9631–9663, DOI: 10.1021/acs.chemrev.5b00694.
- [425] E Herbst and E F van Dishoeck, “Complex Organic Interstellar Molecules”, *Annu Rev Astron Astrophys*, 2009, **47**, 427–480, DOI: 10.1146/annurev-astro-082708-101654.
- [426] A M Turner and R I Kaiser, “Exploiting Photoionization Reflectron Time-of-Flight Mass Spectrometry to Explore Molecular Mass Growth Processes to Complex Organic Molecules in Interstellar and Solar System Ice Analogs”, *Acc Chem Res*, 2020, **53**, 2791–2805, DOI: 10.1021/acs.accounts.0c00584.
- [427] C R Arumainayagam, R T Garrod, M C Boyer, A K Hay, S T Bao, J S Campbell, J Wang, C M Nowak, M R Arumainayagam and P J Hodge, “Extraterrestrial prebiotic molecules: photochemistry vs radiation chemistry of interstellar ices”, *Chem Soc Rev*, 2019, **48**, 2293–2314, DOI: 10.1039/C7CS00443E.
- [428] S A Sandford, M Nuevo, P P Bera and T J Lee, “Prebiotic Astrochemistry and the Formation of Molecules of Astrobiological Interest in Interstellar Clouds and Protostellar Disks”, *Chem Rev*, 2020, **120**, 4616–4659, DOI: 10.1021/acs.chemrev.9b00560.
- [429] K S Noll, H A Weaver and A M Gonnella, “The albedo spectrum of Europa from 2200 Å to 3300 Å”, *J Geophys Res Planets*, 1995, **100**, 19057–19059, DOI: 10.1029/94JE03294.
- [430] K S Noll, R E Johnson, M A McGrath and J J Caldwell, “Detection of SO₂ on Callisto with the Hubble Space Telescope”, *Geophys Res Lett*, 1997, **24**, 1139–1142, DOI: 10.1029/97GL00876. 
- [431] D L Domingue and A L Lane, “IUE views Europa: Temporal variations in the UV”, *Geophys Res Lett*, 1998, **25**, 4421–4424, DOI: 10.1029/1998GL900209. 
- [432] A L Lane and D L Domingue, “IUE’s view of Callisto: Detection of an SO₂ absorption correlated to possible torus neutral wind alterations”, *Geophys Res Lett*, 1997, **24**, 1143–1146, DOI: 10.1029/97GL00884. 
- [433] A Migliorini, Z Kanuchova, S Ioppolo, M Barbieri, N C Jones, S V Hoffmann, G Strazzulla, F Tosi and G Piccioni, “On the origin of molecular oxygen on the surface of Ganymede”, *Icarus*, 2022, **383**, 115074, DOI: 10.1016/j.icarus.2022.115074.

- [434] R Ramachandran, J K Meka, K K Rahul, W Khan, J-I Lo, B-M Cheng, D V Mifsud, B N Rajasekhar, A Das, H Hill, P Janardhan, A Bhardwaj, N J Mason and B Sivaraman, “Ultraviolet spectrum reveals the presence of ozone on Jupiter’s moon Callisto”, *Icarus*, 2024, **410**, 115896, DOI: 10.1016/j.icarus.2023.115896.
- [435] A T Muiña, L E Borchert, Z Kaňuchová, D V Mifsud, **C P Souza**, A M Wilson, A T Hopkinson, M Mikkelsen, J Zhang, J C Santos, J G M Schrauwen, D Ramsamoedj, M Minissale, E Salomon, M Accolla, H Linnartz, B Redlich, M Zlatar, A Dawes, N J Mason, G Strazzulla, N C Jones, S V Hoffmann, L Hornekær, A M Cassidy, M S Gudipati, T Hempel, F Fantuzzi and S Ioppolo, “Survey of the Vacuum-Ultraviolet Spectroscopy and Absorption Cross-Sections of Astrophysical Ice Analogs: A Combined Experimental and Theoretical Study”, Unpublished draft manuscript, 2026.
- [436] F Fantuzzi, J B Maljković, M Zlatar, **C P Souza**, H M Quitián-Lara, P Nag, B Antony, B P Marinković and N J Mason, “Centennial of quantum theory in Belgrade: CEQPAS and the molecular excited state spectroscopy (MOLEsS) initiative”, *J Serb Chem Soc*, 2025, **90**, 1553–1561, DOI: 10.2298/JSC251118083F.
- [437] M B Robin, *Higher Excited States of Polyatomic Molecules*, Academic Press, New York, NY, USA, 1974, vol 1, DOI: 10.1016/B978-0-12-589901-7.X5001-0.
- [438] M B Robin, *Higher Excited States of Polyatomic Molecules*, Academic Press, New York, NY, USA, 1975, vol 2, DOI: 10.1016/B978-0-12-589902-4.X5001-1.
- [439] M B Robin, *Higher Excited States of Polyatomic Molecules*, Academic Press, Orlando, FL, USA, 1985, vol 3, DOI: 10.1016/B978-0-12-589903-1.X5001-2.
- [440] D E Woon, “Benchmarking Time-dependent Density Functional Theory for the prediction of electronic absorption spectra of amorphous ices for astrochemical applications”, *Mol Phys*, 2024, **122**, e2254419, DOI: 10.1080/00268976.2023.2254419.
- [441] J Zhang and M Dolg, “ABCluster: the artificial bee colony algorithm for cluster global optimization”, *Phys Chem Chem Phys*, 2015, **17**, 24173–24181, DOI: 10.1039/C5CP04060D.
- [442] C S Barrett, L Meyer and J Wasserman, “Antiferromagnetic and Crystal Structures of Alpha-Oxygen”, *J Chem Phys*, 1967, **47**, 592–597, DOI: 10.1063/1.1711936.
- [443] Y A Freiman and H J Jodl, “Solid oxygen”, *Phys Rep*, 2004, **401**, 1–228, DOI: 10.1016/j.physrep.2004.06.002.
- [444] M Brith and O Schnepf, “The absorption spectra of solid CO and N₂”, *Mol Phys*, 1965, **9**, 473–489, DOI: 10.1080/00268976500100641.
- [445] J-Y Roncin, N Damany and J Romand, “Far ultraviolet absorption spectra of atoms and molecules trapped in rare gas matrices at low temperature”, *J Mol Spectrosc*, 1967, **22**, 154–164, DOI: 10.1016/0022-2852(67)90161-0.
- [446] S R Scharber Jr and S E Webber, “Optical Constants of Simple Molecular Crystals. I. Results for CO and O₂”, *J Chem Phys*, 1971, **55**, 3977–3985, DOI: 10.1063/1.1676688.
- [447] H-C Lu, H-K Chen, B-M Cheng, Y-P Kuo and J F Ogilvie, “Spectra in the vacuum ultraviolet region of CO in gaseous and solid phases and dispersed in solid argon at 10 K”, *J Phys B: At Mol Opt Phys*, 2005, **38**, 3693, DOI: 10.1088/0953-4075/38/20/006.

- [448] N J Mason, A Dawes, P D Holtom, R J Mukerji, M P Davis, B Sivaraman, R I Kaiser, S V Hoffmann and D A Shaw, "VUV spectroscopy and photo-processing of astrochemical ices: an experimental study", *Faraday Discuss*, 2006, **133**, 311–329, DOI: 10.1039/b518088k.
- [449] G A Cruz-Diaz, G M Muñoz Caro, Y-J Chen and T-S Yih, "Vacuum-UV spectroscopy of interstellar ice analogs II. Absorption cross-sections of nonpolar ice molecules", *A&A*, 2014, **562**, A120, DOI: 10.1051/0004-6361/201322621. 
- [450] G M Muñoz Caro, Y-J Chen, S Aparicio, A Jiménez-Escobar, A Rosu-Finsen, J Lasne and M R S McCoustra, "Photodesorption and physical properties of CO ice as a function of temperature", *A&A*, 2016, **589**, DOI: 10.1051/0004-6361/201628121. 
- [451] R M Hexter, "Forbidden Transitions in Molecular Crystals: The Cameron System of Solid α -CO", *J Chem Phys*, 1967, **46**, 2300–2309, DOI: 10.1063/1.1841036.
- [452] H-C Lu, H-K Chen, B-M Cheng and J Ogilvie, "Absorption spectra in the vacuum ultraviolet region of small molecules in condensed phases", *Spectrochim Acta A Mol Biomol Spectrosc*, 2008, **71**, 1485–1491, DOI: 10.1016/j.saa.2008.05.007.
- [453] G A Cruz-Diaz, G M Muñoz Caro, Y-J Chen and T-S Yih, "Vacuum-UV spectroscopy of interstellar ice analogs I. Absorption cross-sections of polar-ice molecules", *A&A*, 2014, **562**, A119, DOI: 10.1051/0004-6361/201322621.
- [454] K Dressler and O Schnepf, "Absorption Spectra of Solid Methane, Ammonia, and Ice in the Vacuum Ultraviolet", *J Chem Phys*, 1960, **33**, 270–274, DOI: 10.1063/1.1731096.
- [455] A Yabushita, Y Hashikawa, A Ikeda, M Kawasaki and H Tachikawa, "Hydrogen atom formation from the photodissociation of water ice at 193 nm", *J Chem Phys*, 2004, **120**, 5463–5468, DOI: 10.1063/1.1619939.
- [456] A Yabushita, D Kanda, N Kawanaka, M Kawasaki and M N R Ashfold, "Photodissociation of polycrystalline and amorphous water ice films at 157 and 193 nm", *J Chem Phys*, 2006, **125**, 133406, DOI: 10.1063/1.2335840.
- [457] G Avila, G J Kroes and M C van Hemert, "The photodissociation of the water dimer in the $\tilde{A}$ band: A twelve-dimensional quasiclassical study", *J Chem Phys*, 2008, **128**, 144313, DOI: 10.1063/1.2868775.
- [458] H Tachikawa, A Yabushita and M Kawasaki, "Ab initio theoretical calculations of the electronic excitation energies of small water clusters", *Physical Chemistry Chem Phys*, 2011, **13**, 20745–20749, DOI: 10.1039/c1cp20649d.
- [459] M Chergui and N Schwentner, "Experimental evidence to Rydbergization of antibonding molecular orbitals", *Chem Phys Lett*, 1994, **219**, 237–242, DOI: 10.1016/0009-2614(94)87051-9.
- [460] K M Monahan and W C Walker, "Vacuum ultraviolet absorption spectra of solid N₂O and CO₂ at 53 K", *J Chem Phys*, 1975, **63**, 1676–1681, DOI: 10.1063/1.431496.
- [461] S Ioppolo, Z Kaňuchová, R L James, A Dawes, N C Jones, S V Hoffmann, N J Mason and G Strazzulla, "Vacuum ultraviolet photoabsorption spectroscopy of space-related ices: 1 keV electron irradiation of nitrogen- and oxygen-rich ices", *A&A*, 2020, **641**, A154, DOI: 10.1051/0004-6361/201935477. 

- [462] B Sivaraman, B G Nair, B N Raja Sekhar, J-I Lo, R Sridharan, B-M Cheng and N J Mason, “Vacuum ultraviolet photoabsorption of pure solid ozone and its implication on the identification of ozone on Moon”, *Chem Phys Lett*, 2014, **603**, 33–36, DOI: 10.1016/j.cplett.2014.04.021.
- [463] J-I Lo, H-C Lu, W-H Hung, B Sivaraman, N J Mason and B-M Cheng, “Photoabsorption spectra of solid O₂ in ultraviolet and far-vacuum ultraviolet region at 9–30 K”, *Mon Not R Astron Soc*, 2024, **529**, 4818–4823, DOI: 10.1093/mnras/stae779. 
- [464] A Grill, “Diamond-like carbon: state of the art”, *Diam Relat Mater*, 1999, **8**, 428–434, DOI: 10.1016/S0925-9635(98)00262-3.
- [465] D D L Chung, “Review Graphite”, *J Mater Sci*, 2002, **37**, 1475–1489, DOI: 10.1023/A:1014915307738.
- [466] V Popov, “Carbon nanotubes: properties and application”, *Mater Sci Eng R Reports*, 2004, **43**, 61–102, DOI: 10.1016/j.mser.2003.10.001.
- [467] H W Kroto, “The stability of the fullerenes C_n, with $n = 24, 28, 32, 36, 50, 60$ and 70”, *Nature*, 1987, **329**, 529–531, DOI: 10.1038/329529a0.
- [468] R Taylor and D R M Walton, “The chemistry of fullerenes”, *Nature*, 1993, **363**, 685–693, DOI: 10.1038/363685a0.
- [469] A K Geim, “Graphene: Status and Prospects”, *Science*, 2009, **324**, 1530–1534, DOI: 10.1126/science.1158877.
- [470] C-H Park, L Yang, Y-W Son, M L Cohen and S G Louie, “Anisotropic behaviours of massless Dirac fermions in graphene under periodic potentials”, *Nat Phys*, 2008, **4**, 213–217, DOI: 10.1038/nphys890.
- [471] K S Novoselov, A K Geim, S V Morozov, D Jiang, M I Katsnelson, I V Grigorieva, S V Dubonos and A A Firsov, “Two-dimensional gas of massless Dirac fermions in graphene”, *Nature*, 2005, **438**, 197–200, DOI: 10.1038/nature04233.
- [472] R S Shishir and D K Ferry, “Intrinsic mobility in graphene”, *J Phys Condens Matter*, 2009, **21**, 232204, DOI: 10.1088/0953-8984/21/23/232204.
- [473] K Bolotin, “Electronic transport in graphene: towards high mobility”, in *Graphene*, ed V Skákalová and A B Kaiser, Woodhead Publishing, Cambridge, 2014, pp 199–227, DOI: 10.1533/9780857099334.3.199.
- [474] H Hirai, H Tsuchiya, Y Kamakura, N Mori and M Ogawa, “Electron mobility calculation for graphene on substrates”, *J Appl Phys*, 2014, **116**, DOI: 10.1063/1.4893650.
- [475] A A Balandin, S Ghosh, W Bao, I Calizo, D Teweldebrhan, F Miao and C N Lau, “Superior Thermal Conductivity of Single-Layer Graphene”, *Nano Lett*, 2008, **8**, 902–907, DOI: 10.1021/nl0731872.
- [476] H Malekpour, K-H Chang, J-C Chen, C-Y Lu, D L Nika, K S Novoselov and A A Balandin, “Thermal Conductivity of Graphene Laminate”, *Nano Lett*, 2014, **14**, 5155–5161, DOI: 10.1021/nl501996v.

- [477] T Y Kim, C-H Park and N Marzari, “The Electronic Thermal Conductivity of Graphene”, *Nano Lett*, 2016, **16**, 2439–2443, DOI: 10.1021/acs.nanolett.5b05288.
- [478] M H Kang, L O Prieto López, B Chen, K Teo, J A Williams, W I Milne and M T Cole, “Mechanical Robustness of Graphene on Flexible Transparent Substrates”, *ACS Appl Mater Interfaces*, 2016, **8**, 22506–22515, DOI: 10.1021/acsami.6b06557.
- [479] S Chen, Q Lin, Z Ji, Z Sun and B Shen, “Ultrahigh mechanical robustness of vertical graphene sheets covalently bonded to diamond”, *Carbon NY*, 2023, **201**, 390–398, DOI: 10.1016/j.carbon.2022.09.046.
- [480] R Geetha Bai, N Ninan, K Muthoosamy and S Manickam, “Graphene: A versatile platform for nanotheranostics and tissue engineering”, *Prog Mater Sci*, 2018, **91**, 24–69, DOI: 10.1016/j.pmatsci.2017.08.004.
- [481] R Maheswaran and B P Shanmugavel, “A Critical Review of the Role of Carbon Nanotubes in the Progress of Next-Generation Electronic Applications”, *J Electron Mater*, 2022, **51**, 2786–2800, DOI: 10.1007/s11664-022-09516-8.
- [482] F Bonaccorso, Z Sun, T Hasan and A C Ferrari, “Graphene photonics and optoelectronics”, *Nat Photonics*, 2010, **4**, 611–622, DOI: 10.1038/nphoton.2010.186.
- [483] X Wan, Y Huang and Y Chen, “Focusing on Energy and Optoelectronic Applications: A Journey for Graphene and Graphene Oxide at Large Scale”, *Acc Chem Res*, 2012, **45**, 598–607, DOI: 10.1021/ar200229q.
- [484] Q Bao and K P Loh, “Graphene Photonics, Plasmonics, and Broadband Optoelectronic Devices”, *ACS Nano*, 2012, **6**, 3677–3694, DOI: 10.1021/nn300989g.
- [485] W Han, R K Kawakami, M Gmitra and J Fabian, “Graphene spintronics”, *Nat Nanotechnol*, 2014, **9**, 794–807, DOI: 10.1038/nnano.2014.214.
- [486] S Roche, J Åkerman, B Beschoten, J-C Charlier, M Chshiev, S Prasad Dash, B Dlubak, J Fabian, A Fert, M Guimarães, F Guinea, I Grigorieva, C Schönenberger, P Seneor, C Stampfer, S O Valenzuela, X Waintal and B van Wees, “Graphene spintronics: the European Flagship perspective”, *2D Mater*, 2015, **2**, 030202, DOI: 10.1088/2053-1583/2/3/030202.
- [487] S Stankovich, D A Dikin, G H B Dommett, K M Kohlhaas, E J Zimney, E A Stach, R D Piner, S T Nguyen and R S Ruoff, “Graphene-based composite materials”, *Nature*, 2006, **442**, 282–286, DOI: 10.1038/nature04969.
- [488] X Li, J Yu, S Wageh, A A Al-Ghamdi and J Xie, “Graphene in Photocatalysis: A Review”, *Small*, 2016, **12**, 6640–6696, DOI: 10.1002/smll.201600382.
- [489] A Kuc, T Heine and G Seifert, “Structural and electronic properties of graphene nanoflakes”, *Phys Rev B*, 2010, **81**, 085430, DOI: 10.1103/PhysRevB.81.085430.
- [490] M Bacon, S J Bradley and T Nann, “Graphene Quantum Dots”, *Part Part Syst Charact*, 2014, **31**, 415–428, DOI: 10.1002/ppsc.201300252.
- [491] W L Wang, S Meng and E Kaxiras, “Graphene NanoFlakes with Large Spin”, *Nano Lett*, 2008, **8**, 241–245, DOI: 10.1021/nl072548a.

- [492] H Shi, A S Barnard and I K Snook, “Quantum mechanical properties of graphene nano-flakes and quantum dots”, *Nanoscale*, 2012, **4**, 6761, DOI: 10.1039/c2nr31354e.
- [493] M N Norizan, M H Moklis, S Z Ngah Demon, N A Halim, A Samsuri, I S Mohamad, V F Knight and N Abdullah, “Carbon nanotubes: functionalisation and their application in chemical sensors”, *RSC Adv*, 2020, **10**, 43704–43732, DOI: 10.1039/D0RA09438B.
- [494] M H M Facure, R Schneider, L A Mercante and D S Correa, “A review on graphene quantum dots and their nanocomposites: from laboratory synthesis towards agricultural and environmental applications”, *Environ Sci Nano*, 2020, **7**, 3710–3734, DOI: 10.1039/D0EN00787K.
- [495] P Tian, L Tang, K Teng and S Lau, “Graphene quantum dots from chemistry to applications”, *Mater Today Chem*, 2018, **10**, 221–258, DOI: 10.1016/j.mtchem.2018.09.007.
- [496] E O Pentsak, E G Gordeev and V P Ananikov, “Noninnocent Nature of Carbon Support in Metal/Carbon Catalysts: Etching/Pitting vs Nanotube Growth under Microwave Irradiation”, *ACS Catal*, 2014, **4**, 3806–3814, DOI: 10.1021/cs500934g.
- [497] B P Uberuaga, S J Stuart, W Windl, M P Masquelier and A F Voter, “Fullerene and graphene formation from carbon nanotube fragments”, *Comput Theor Chem*, 2012, **987**, 115–121, DOI: 10.1016/j.comptc.2011.11.030.
- [498] F Pietrucci and W Andreoni, “Fate of a Graphene Flake: A New Route toward Fullerenes Disclosed with Ab Initio Simulations”, *J Chem Theory Comput*, 2014, **10**, 913–917, DOI: 10.1021/ct401103p.
- [499] A Chuvilin, U Kaiser, E Bichoutskaia, N A Besley and A N Khlobystov, “Direct transformation of graphene to fullerene”, *Nat Chem*, 2010, **2**, 450–453, DOI: 10.1038/nchem.644.
- [500] M Bachmann, W Wiese and K-H Homann, “PAH and aromers: Precursors of fullerenes and soot”, *Symp Combust*, 1996, **26**, 2259–2267, DOI: 10.1016/S0082-0784(96)80053-1.
- [501] B Wu, L Jiang, Y Luo and C Wang, “The Effect of the Polyaromatic Hydrocarbon in the Formation of Fullerenes”, *Angew Chem Int Ed*, 2020, **59**, 3942–3947, DOI: 10.1002/anie.201915228.
- [502] S Ahmad, K Mustonen, B McLean, H Jiang, Q Zhang, A Hussain, A T Khan, E-X Ding, Y Liao, N Wei, M R A Monazam, A G Nasibulin, J Kotakoski, A J Page and E I Kauppinen, “Hybrid Low-Dimensional Carbon Allotropes Formed in Gas Phase”, *Adv Funct Mater*, 2020, **30**, DOI: 10.1002/adfm.202005016.
- [503] J Ma, D Alfè, A Michaelides and E Wang, “Stone-Wales defects in graphene and other planar sp²-bonded materials”, *Phys Rev B*, 2009, **80**, 033407, DOI: 10.1103/PhysRevB.80.033407.
- [504] I M Macías Labrada, L I Estévez Baños, D Codorniu Pujals and M Márquez Mijares, “Carbon nanotubes with point defects produced by ionizing radiation: a study using DFTB”, *Eur Phys J D*, 2023, **77**, 153, DOI: 10.1140/epjd/s10053-023-00735-0.
- [505] G P Nogueira Lima, R R Oliveira and P M Esteves, “A combination of normal vibrational modes as triggers to phase transitions between carbon allotropes”, *Carbon NY*, 2026, **250**, 121271, DOI: 10.1016/j.carbon.2026.121271.

- [506] A S Barnard and I K Snook, “Thermal stability of graphene edge structure and graphene nanoflakes”, *J Chem Phys*, 2008, **128**, 094707, DOI: 10.1063/1.2841366.
- [507] E Surdutovich, A V Yakubovich and A V Solov'yov, “Biodamage via shock waves initiated by irradiation with ions”, *Sci Rep*, 2013, **3**, 1289, DOI: 10.1038/srep01289.
- [508] E Surdutovich and A V Solov'yov, “Multiscale approach to the physics of radiation damage with ions”, *Eur Phys J D*, 2014, **68**, 353, DOI: 10.1140/epjd/e2014-50004-0.
- [509] I Friis, A V Verkhovtsev, I A Solov'yov and A V Solov'yov, “Lethal DNA damage caused by ion-induced shock waves in cells”, *Phys Rev E*, 2021, **104**, 054408, DOI: 10.1103/PhysRevE.104.054408.
- [510] A V Verkhovtsev, A V Korol and A V Solov'yov, “Classical molecular dynamics simulations of fusion and fragmentation in fullerene-fullerene collisions”, *Eur Phys J D*, 2017, **71**, 212, DOI: 10.1140/epjd/e2017-80117-7.
- [511] A G G M Tielens, *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, Cambridge, MA, USA, 2005, DOI: 10.1017/CB09780511819056.
- [512] K He, G-D Lee, A W Robertson, E Yoon and J H Warner, “Hydrogen-free graphene edges”, *Nat Commun*, 2014, **5**, 3040, DOI: 10.1038/ncomms4040.
- [513] S Schneider and R Hoffmann-Vogel, “Electrostatic forces above graphene nanoribbons and edges interpreted as partly hydrogen-free”, *Nanoscale*, 2020, **12**, 17895–17901, DOI: 10.1039/D0NR03348K.
- [514] R Brandolt and R Paupitz, “Theoretical study of collision dynamics of fullerenes on graphenylene and porous graphene membranes”, *J Mol Graph Model*, 2020, **100**, 107664, DOI: 10.1016/j.jmgm.2020.107664.
- [515] A S Barnard, B Sun and H R Shi, *Graphene Nanoflake Data Set*, ver v1, CSIRO Data Collection, 2016, DOI: 10.4225/08/57998CC4D7891.
- [516] D W Brenner, “Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films”, *Phys Rev B*, 1990, **42**, 9458–9471, DOI: 10.1103/PhysRevB.42.9458.
- [517] J Geng, I A Solov'yov, W Zhou, A V Solov'yov and B F G Johnson, “Uncovering a Solvent-Controlled Preferential Growth of Buckminsterfullerene (C₆₀) Nanowires”, *J Phys Chem C*, 2009, **113**, 6390–6397, DOI: 10.1021/jp809664g.
- [518] K Cielinska, A V Verkhovtsev, **C P Souza**, M D Dickers, A V Solov'yov, N J Mason and F Fantuzzi, “Unpassivated edges as gateways to collision-driven topological transformations in finite graphene nanoflakes”, *The European Physical Journal D*, 2026, **80**, 134, DOI: 10.1140/epjd/s10053-026-01242-8.
- [519] J Wahlers, A R Rosales, N Berkel, A Forbes, P Helquist, P-O Norrby and O Wiest, “A Quantum-Guided Molecular Mechanics Force Field for the Ferrocene Scaffold”, *J Org Chem*, 2022, **87**, 12334–12341, DOI: 10.1021/acs.joc.2c01553.

- [520] D P White and T L Brown, “Molecular Mechanics Model of Ligand Effects 7. Binding of η^2 Ligands to $\text{Cr}(\text{CO})_5$ and $\text{CpRh}(\text{CO})$: ER Values for Olefins”, *Inorg Chem*, 1995, **34**, 2718–2724, DOI: 10.1021/ic00114a034.
- [521] P O Norrby, B Aakermark, F Haefner, S Hansson and M Blomberg, “Molecular mechanics (MM2) parameters for the η^3 -allylpalladium moiety”, *J Am Chem Soc*, 1993, **115**, 4859–4867, DOI: 10.1021/ja00064a054.
- [522] N Fey, “Organometallic molecular modelling – the computational chemistry of metallocenes: a review”, *J Chem Technol Biotechnol*, 1999, **74**, 852–862, DOI: 10.1002/(SICI)1097-4660(199909)74:9<852::AID-JCTB131>3.0.CO;2-T.
- [523] J M Seminario, “Calculation of intramolecular force fields from second-derivative tensors”, *Int J Quantum Chem*, 1996, **60**, 1271–1277, DOI: 10.1002/(SICI)1097-461X(1996)60:7<1271::AID-QUA8>3.0.CO;2-W.
- [524] S Zheng, Q Tang, J He, S Du, S Xu, C Wang, Y Xu and F Lin, “VFFDT: A New Software for Preparing AMBER Force Field Parameters for Metal-Containing Molecular Systems”, *J Chem Inf Model*, 2016, **56**, 811–818, DOI: 10.1021/acs.jcim.5b00687.
- [525] M Barbatti, “Nonadiabatic dynamics with trajectory surface hopping method”, *WIREs Comput Mol Sci*, 2011, **1**, 620–633, DOI: 10.1002/wcms.64.
- [526] M T. do Casal, J Toldo, M Pinheiro Jr and M Barbatti, “Fewest switches surface hopping with Baek-An couplings [version 2; peer review: 3 approved]”, *Open Res Eur*, 2022, **1**, DOI: 10.12688/openreseurope.13624.2.
- [527] R Crespo-Otero and M Barbatti, “Recent Advances and Perspectives on Nonadiabatic Mixed Quantum–Classical Dynamics”, *Chem Rev*, 2018, **118**, 7026–7068, DOI: 10.1021/acs.chemrev.7b00577.
- [528] T R Nelson, A J White, J A Bjorgaard, A E Sifain, Y Zhang, B Nebgen, S Fernandez-Alberti, D Mozyrsky, A E Roitberg and S Tretiak, “Non-adiabatic Excited-State Molecular Dynamics: Theory and Applications for Modeling Photophysics in Extended Molecular Materials”, *Chem Rev*, 2020, **120**, 2215–2287, DOI: 10.1021/acs.chemrev.9b00447.
- [529] M Persico and G Granucci, “An overview of nonadiabatic dynamics simulations methods, with focus on the direct approach versus the fitting of potential energy surfaces”, *Theor Chem Acc*, 2014, **133**, 1526, DOI: 10.1007/s00214-014-1526-1.
- [530] F Plasser, M Barbatti, A J A Aquino and H Lischka, “Electronically excited states and photodynamics: a continuing challenge”, *Theor Chem Acc*, 2012, **131**, 1073, DOI: 10.1007/s00214-011-1073-y.
- [531] S Hammes-Schiffer, “Theoretical perspectives on non-Born–Oppenheimer effects in chemistry”, *Philos Trans R Soc A Math Phys Eng Sci*, 2022, **380**, 20200377, DOI: 10.1098/rsta.2020.0377.
- [532] J Coonjobeehar, K E Spinlove, C Sanz Sanz, M Sapunar, N Došlić and G A Worth, “Mixed-quantum-classical or fully-quantized dynamics? A unified code to compare methods”, *Philos Trans R Soc A Math Phys Eng Sci*, 2022, **380**, 20200386, DOI: 10.1098/rsta.2020.0386.

- [533] M Maiuri, M Garavelli and G Cerullo, “Ultrafast Spectroscopy: State of the Art and Open Challenges”, *J Am Chem Soc*, 2020, **142**, 3–15, DOI: 10.1021/jacs.9b10533.
- [534] I Conti, G Cerullo, A Nenov and M Garavelli, “Ultrafast Spectroscopy of Photoactive Molecular Systems from First Principles: Where We Stand Today and Where We Are Going”, *J Am Chem Soc*, 2020, **142**, 16117–16139, DOI: 10.1021/jacs.0c04952.
- [535] A S Petit and J E Subotnik, “Calculating time-resolved differential absorbance spectra for ultrafast pump-probe experiments with surface hopping trajectories”, *J Chem Phys*, 2014, **141**, 154108, DOI: 10.1063/1.4897258.
- [536] J P Zobel and L González, “The Quest to Simulate Excited-State Dynamics of Transition Metal Complexes”, *JACS Au*, 2021, **1**, 1116–1140, DOI: 10.1021/jacsau.1c00252.
- [537] **C P Souza**, A V Verkhovtsev, N J Mason, A V Solov’yov and F Fantuzzi, “A refined atomistic model of functionalized self-assembled monolayers on gold: Assessment of force field parameters”, *J Chem Phys*, 2025, **163**, 094704, DOI: 10.1063/5.0274290.
- [538] B Ikenson, “Advancing the understanding of self-assembled monolayers”, *Scilight*, 2025, **2025**, 361105, DOI: 10.1063/10.0039292.
- [539] **C P Souza** and F Fantuzzi, “Condensed-phase effects in the vacuum-ultraviolet spectra of H₂O and O₂ interstellar ice analogues”, *EPJ Web Conf*, 2026, **382**, 05003, DOI: 10.1051/epjconf/202638205003.
- [540] V S A Bonfim, **C P Souza**, D A B de Oliveira, L Baptista, A C F Santos and F Fantuzzi, “Deciphering the irradiation induced fragmentation–rearrangement mechanisms in valence ionized CF₃CH₂F”, *J Chem Phys*, 2024, **160**, 124308, DOI: 10.1063/5.0188201.
- [541] J C de Oliveira, B U Abreu, E R S Paz, R G Almeida, J Honorato, **C P Souza**, F Fantuzzi, V F S Ramos, R F S Menna-Barreto, M H Araujo, G A M Jardim and E N da Silva Júnior, “SuFEx-Functionalized Quinones via Ruthenium-Catalyzed C–H Alkenylation: A Potential Building Block for Bioactivity Valorization”, *Chem Asian J*, 2024, **19**, e202400757, DOI: 10.1002/asia.202400757.
- [542] Y He, **C P Souza**, J Weiser, M Dietz, I Krummenacher, R D Dewhurst, H Braunschweig, F Fantuzzi and J Cui, “Single-Electron Oxidation, Chloride Abstraction, and Hydride-Induced Decomposition of a Dichloro-Bis(Germylene)”, *Eur J Inorg Chem*, 2024, **27**, e202400422, DOI: 10.1002/ejic.202400422.
- [543] D Das, A Roy, **C P Souza**, S Mondal, S Sutradhar, P Sarkar, F Fantuzzi and B N Ghosh, “A copper complex receptor for nanomolar sulfide sensing and applications in DNA/BSA binding”, *J Photochem Photobiol A*, 2025, **461**, 116154, DOI: 10.1016/j.jphotochem.2024.116154.
- [544] E R S Paz, **C P Souza**, J C de Oliveira, R G Almeida, C Herrera-Acevedo, S Lakoh, G A M Jardim, E N da Silva Júnior and F Fantuzzi, “Ruthenium-Catalyzed C–H Alkenylation of Trypanocidal Naphthoquinones: A Mechanistic Benchmarking Study”, *ChemistryOpen*, 2026, **15**, e202500465, DOI: 10.1002/open.202500465.

- [545] A Marulanda-Gallego, **C P Souza** and F Fantuzzi, “Local structural effects on the VUV absorption of H₂S ice models: A TD-DFT cluster investigation”, *EPJ Web Conf*, 2026, **382**, 05002, DOI: 10.1051/epjconf/202638205002.



APPENDIX A

SUPPLEMENTARY DATA FOR PHOTOCHEMISTRY OF PACVD PRECURSORS (CHAPTER 3)

A.1 SIMULATED SPECTRA AND PRISTINE PRECURSORS NTOS

FIGURE 3.7 PRESENTS ALL calculated spectra of pristine precursors and a selected set of NTOS. Here, we supplement this data with the addition of calculated fragment spectra for each of the precursors **3COT**, **3BuD**, and **3CBuD** and for $\text{Ru}(\text{CO})_n$ ($n = 3, 2, 1$). To support the transition character assignments given in Table 3.6, NTOS for each relevant transition in the pristine precursors are also presented.

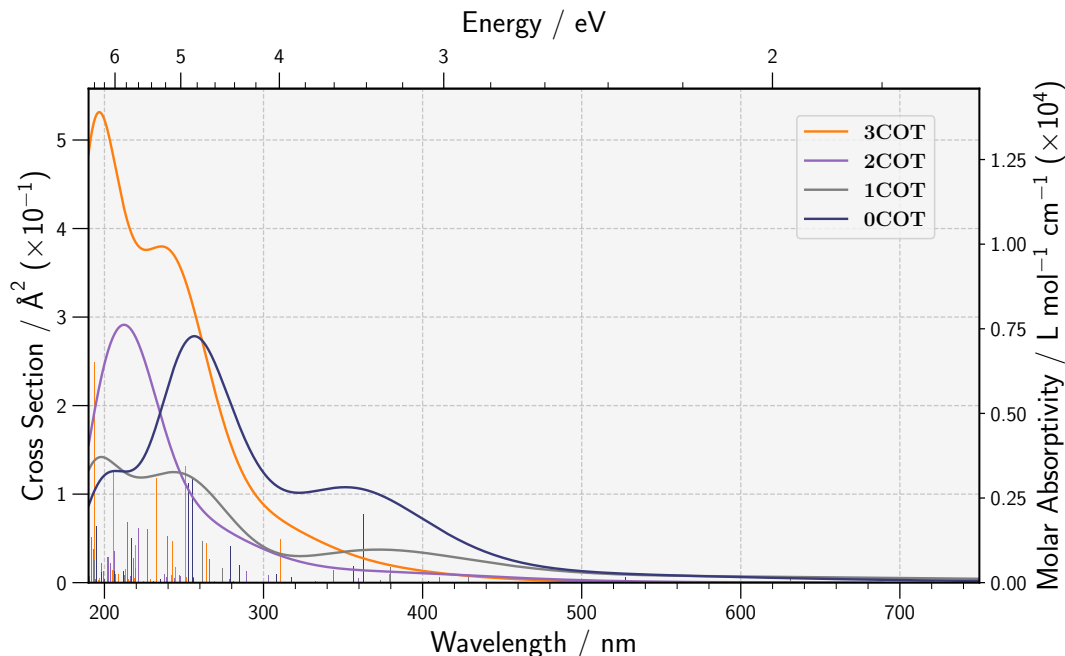


FIGURE A.1 – Calculated spectra for intact **3COT** and its diene-containing fragments. The spectral envelopes are Gaussians with $\sigma = 0.4$ eV. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP.

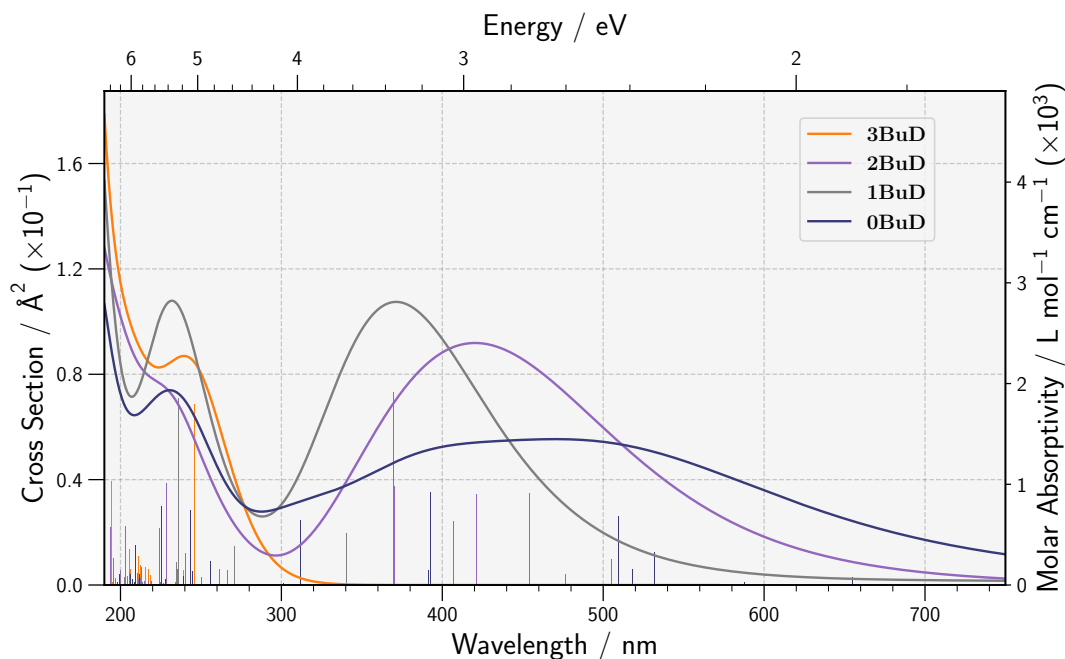


FIGURE A.2 – Calculated spectra for intact **3BuD** and its diene-containing fragments. The spectral envelopes are Gaussians with $\sigma = 0.4$ eV. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP.

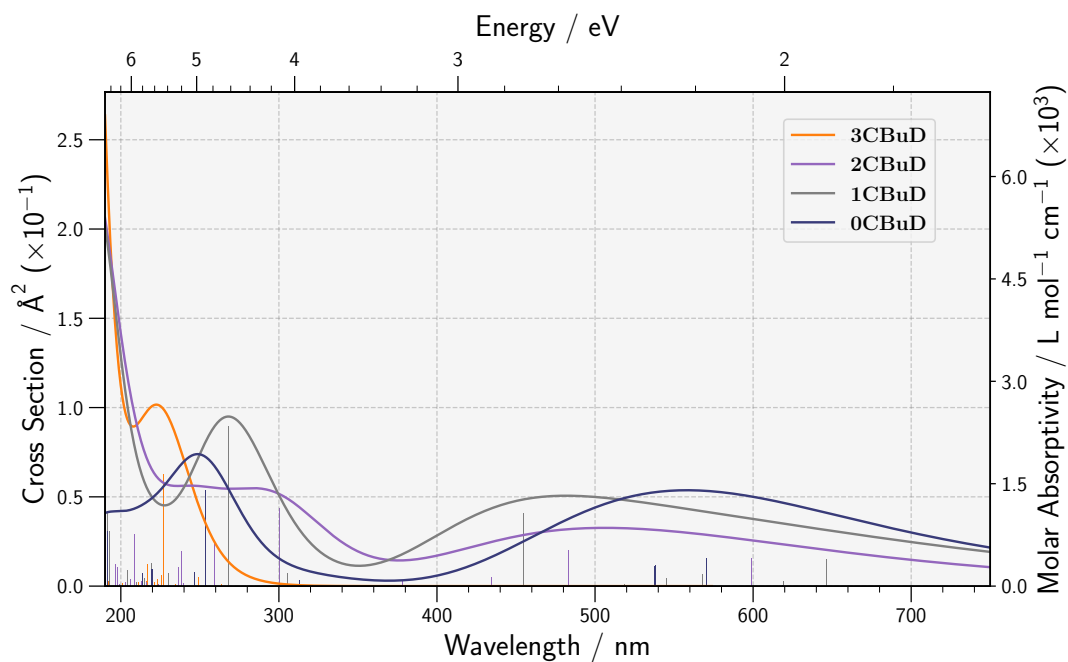


FIGURE A.3 – Calculated spectra for intact **3CBuD** and its diene-containing fragments. The spectral envelopes are Gaussians with $\sigma = 0.4$ eV. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

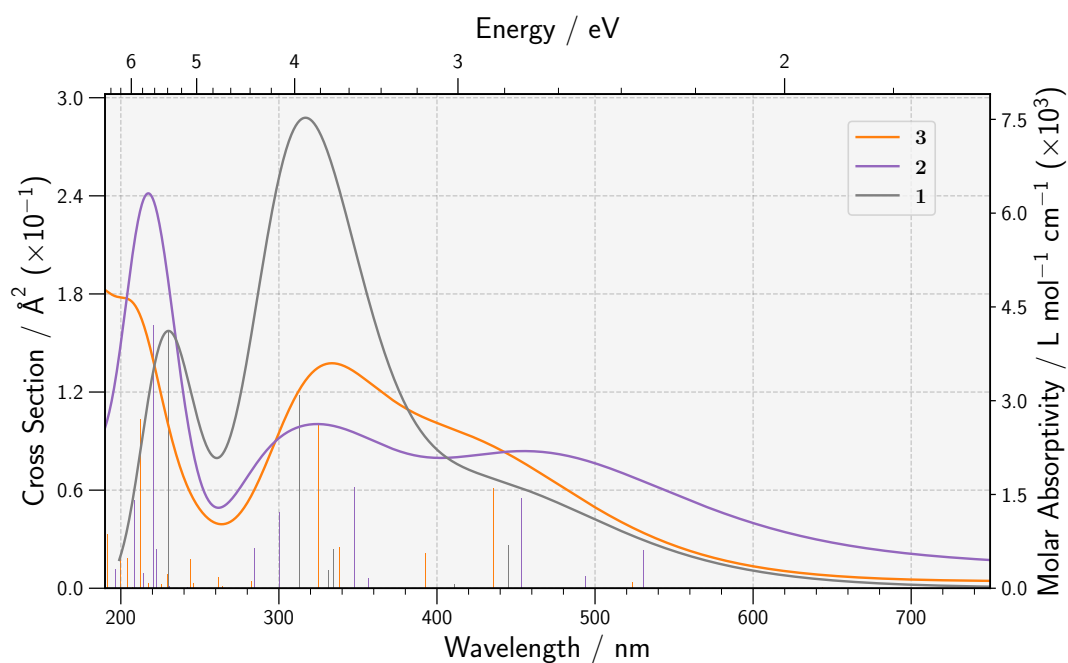


FIGURE A.4 – Calculated spectra for $\text{Ru}(\text{CO})_n$ ($n = 3, 2, 1$) fragments. The spectral envelopes are Gaussians with $\sigma = 0.4$ eV. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

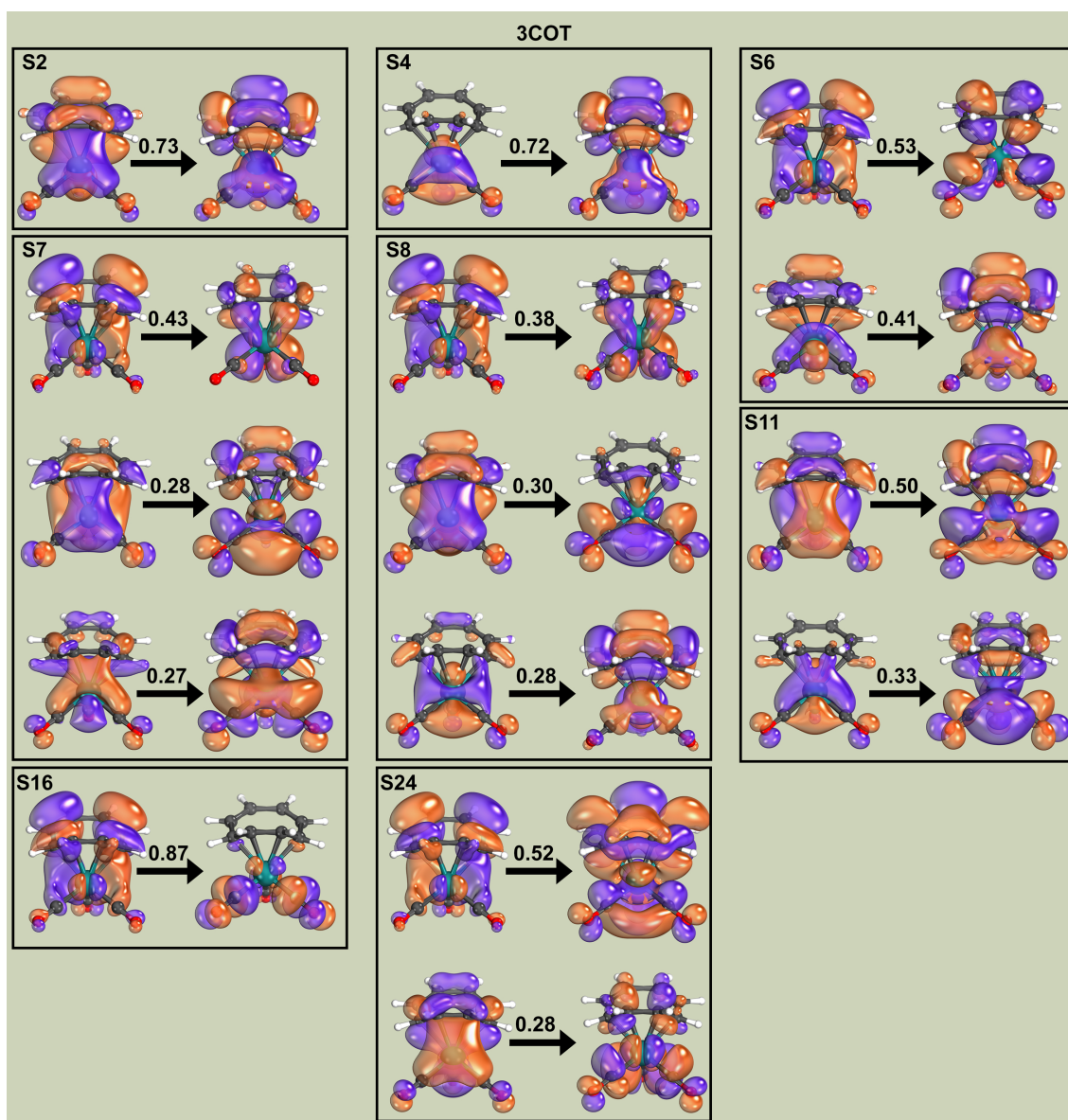


FIGURE A.5 – Main NTO components for all electronic transitions in **3COT** as presented in Table 3.6. Values over the arrows are the electronic occupation transfer associated with each transition orbital pair. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP. Plots represent 80% of the density.

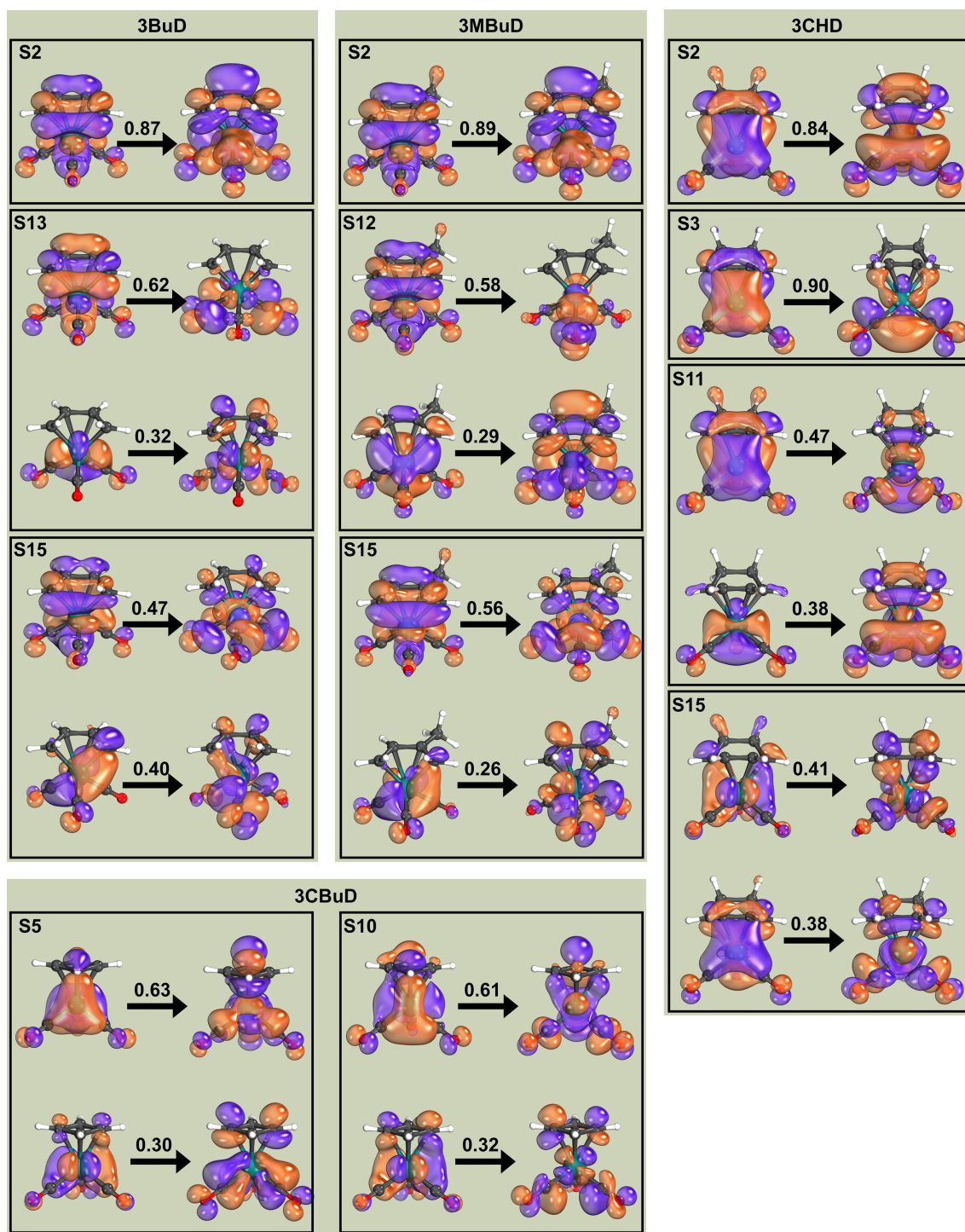


FIGURE A.6 – Main NTO components for all electronic transitions in pristine precursors other than **3cot** (see Figure A.5) as presented in Table 3.6. Values over the arrows are the electronic occupation transfer associated with each transition orbital pair. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP. Plots represent 80% of the density.

A.2 FULL SET OF SCANS AND NEB MEP WITH SUPPORTING NTOs

IN THIS SECTION, WE COLLECT all the rigid scans and NEB MEP generated in this investigation. Figure A.9 offers a schematic representation of the NEB MEP to help in visualising its positioning in relationship to the dissociation of the Ru–diene bond and the distortion of the diene ligand from its bonded geometry to its isolated relaxed geometry.

A.2.1 3COT

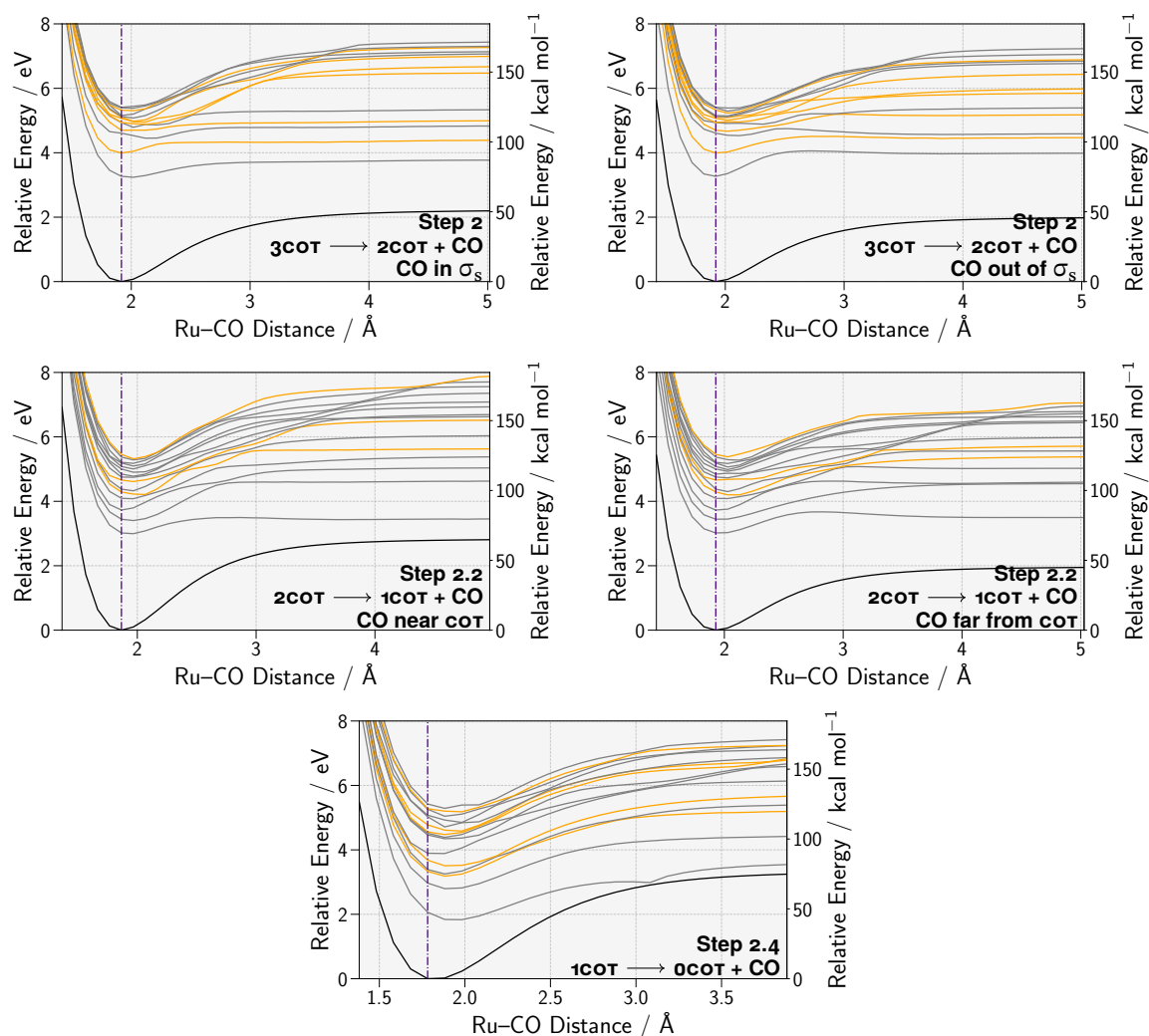


FIGURE A.7 – Rigid scans for Ru–CO dissociation in 3COT and its fragments. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ $\omega\text{B97X-D3/def2-sVP, def2-TZVP(Ru)} + \text{ECP}$.

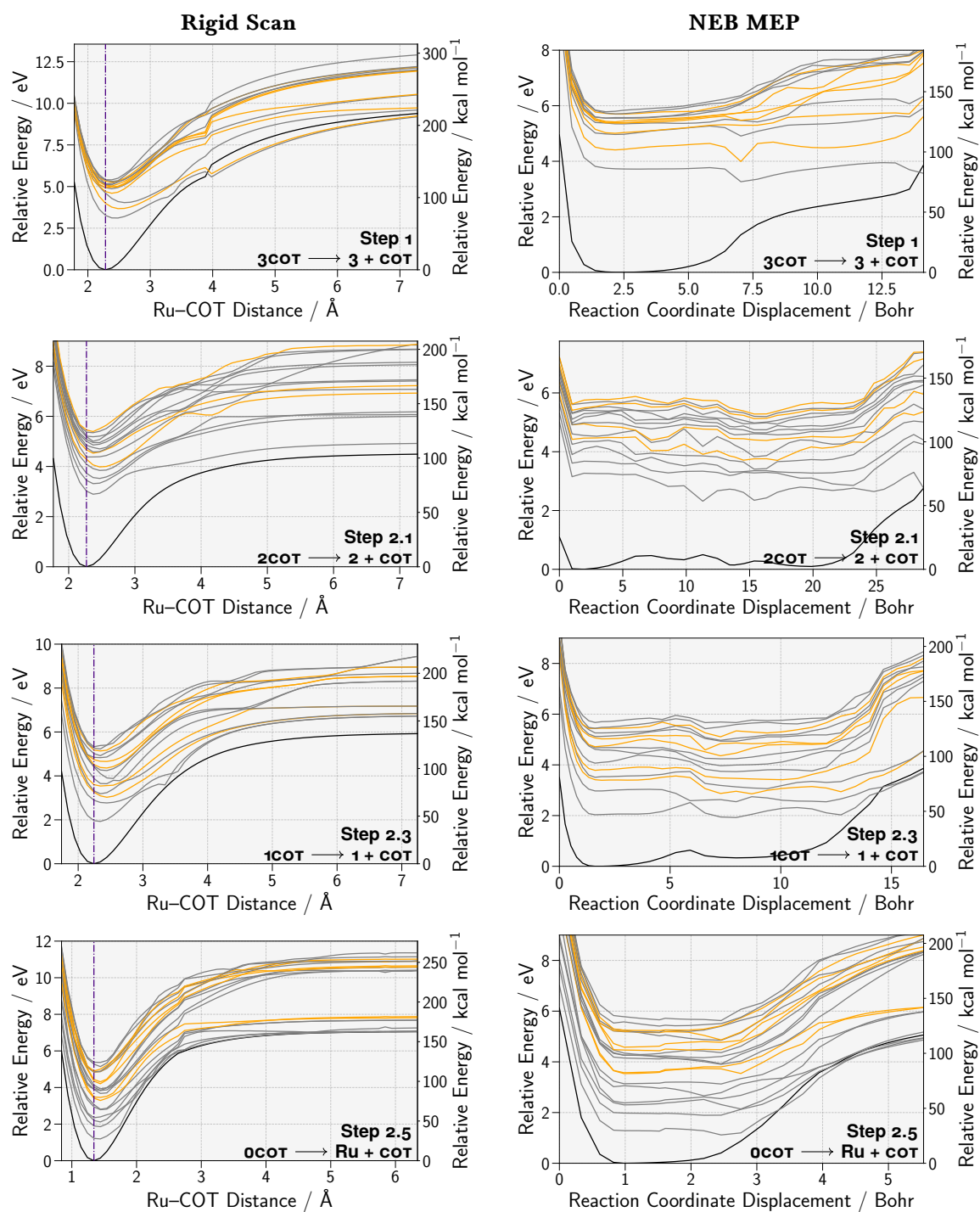


FIGURE A.8 – Rigid scans and NEB MEPs for Ru-COT dissociation in **3COT** and its fragments. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP. See Figure A.9 for a schematic visualisation of the NEB MEPs.

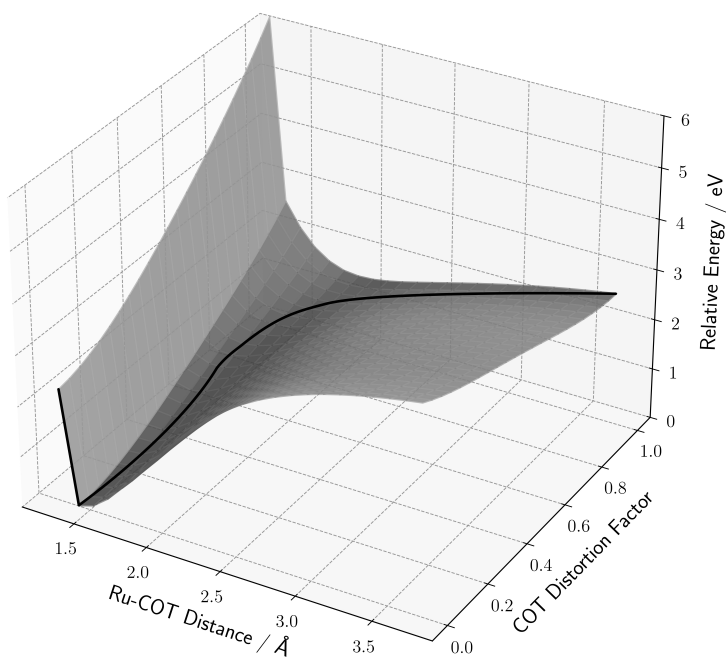


FIGURE A.9 – Schematic representation of the MEP obtained by a NEB calculation (black curve, as in Figure A.8 and Figure A.14) superimposed on a bidimensional GS PES slice (grey surface) in which the diene is simultaneously dissociated from the metal and distorted from its bonded geometry to its isolated relaxed geometry.

A.2.2 3CHD

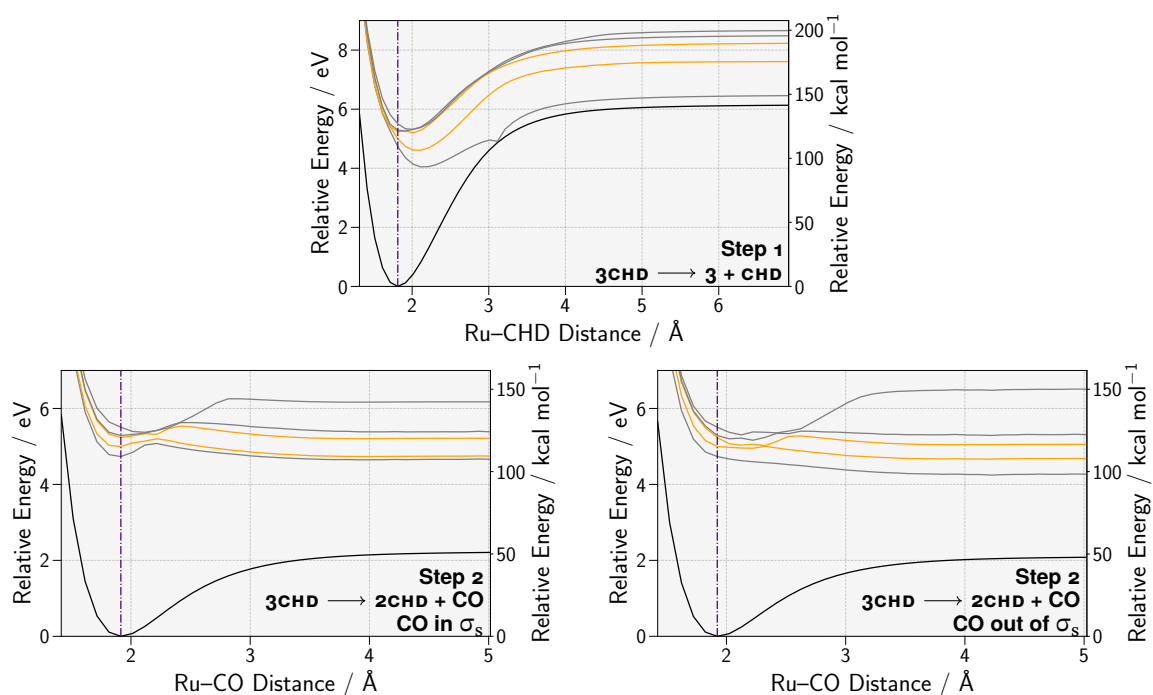


FIGURE A.10 – Rigid scans for Ru-CHD and Ru-CO dissociation in 3CHD . Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ $\omega\text{B97X-D3/def2-svp, def2-TZVP(Ru)} + \text{ECP}$.

A.2.3 3BuD

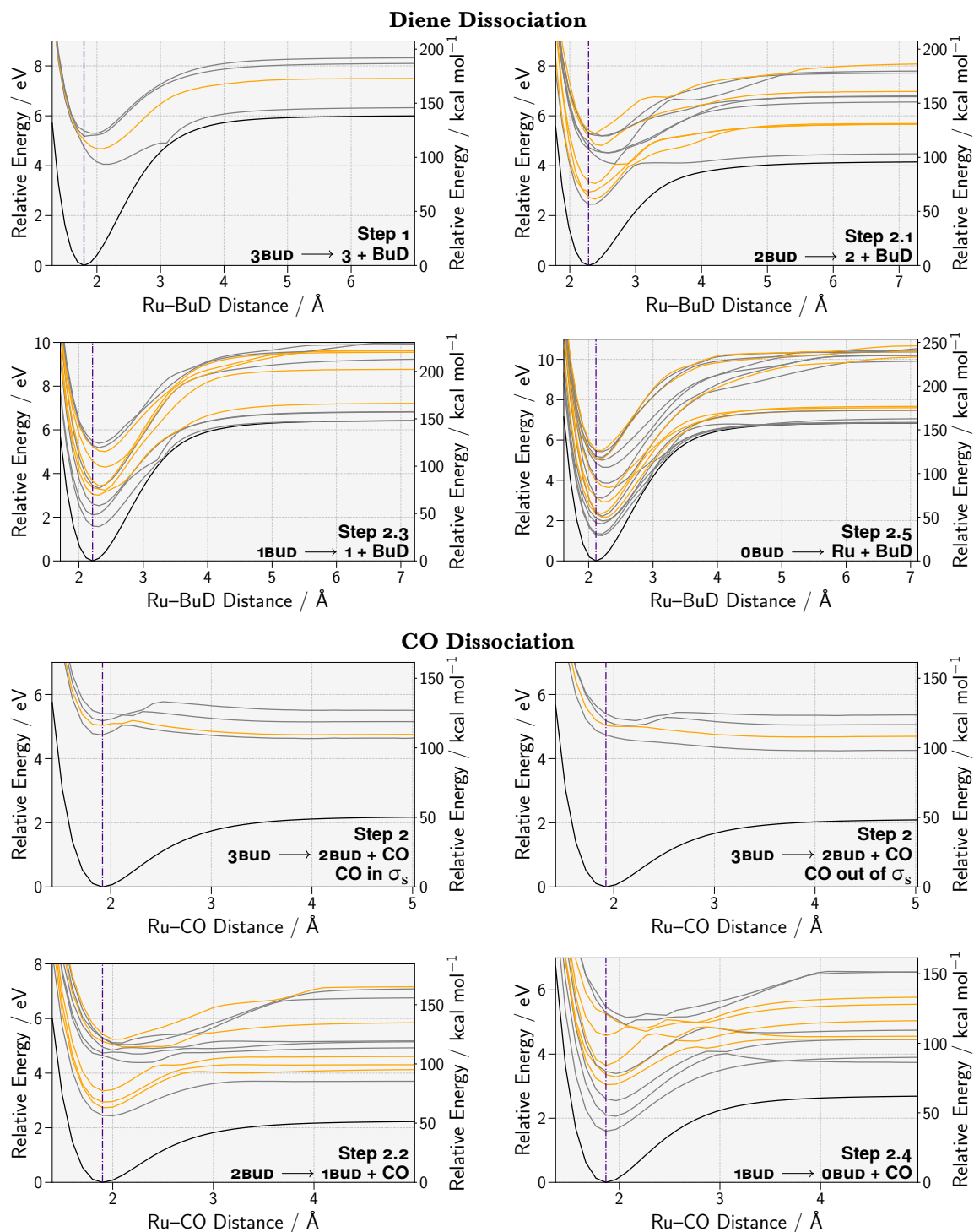


FIGURE A.11 – Rigid scans for Ru–CO dissociation in **3BuD** and its fragments. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP.

A.2.4 3MBuD

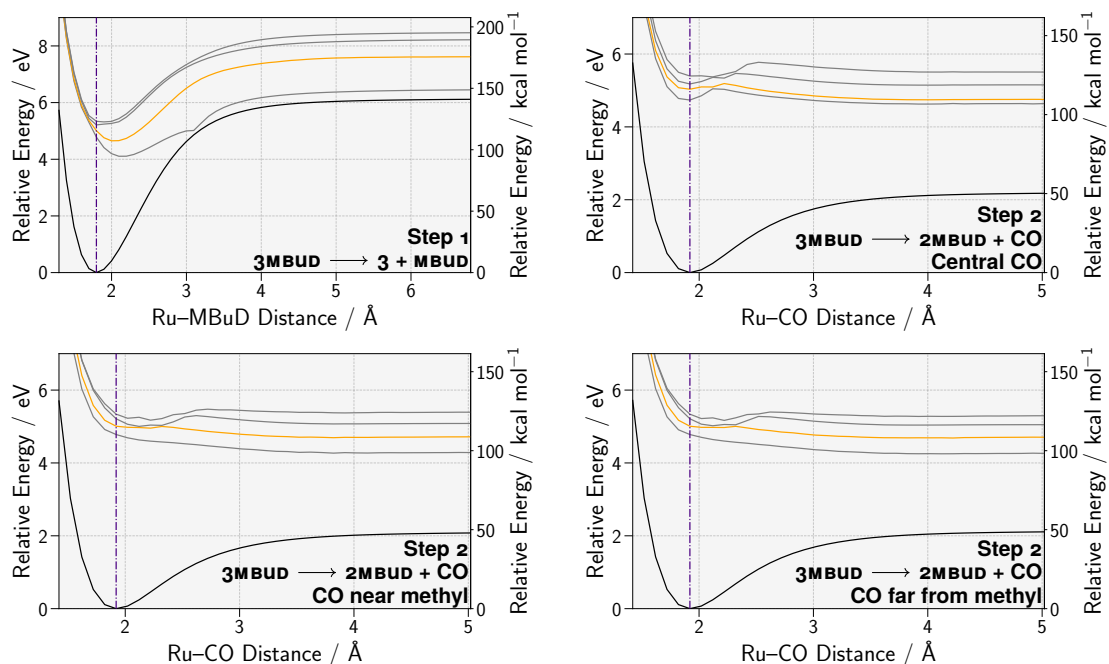


FIGURE A.12 – Rigid scans for Ru-MBuD and Ru-CO dissociation in **3MBuD**. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PES. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP.

A.2.5 3CBuD

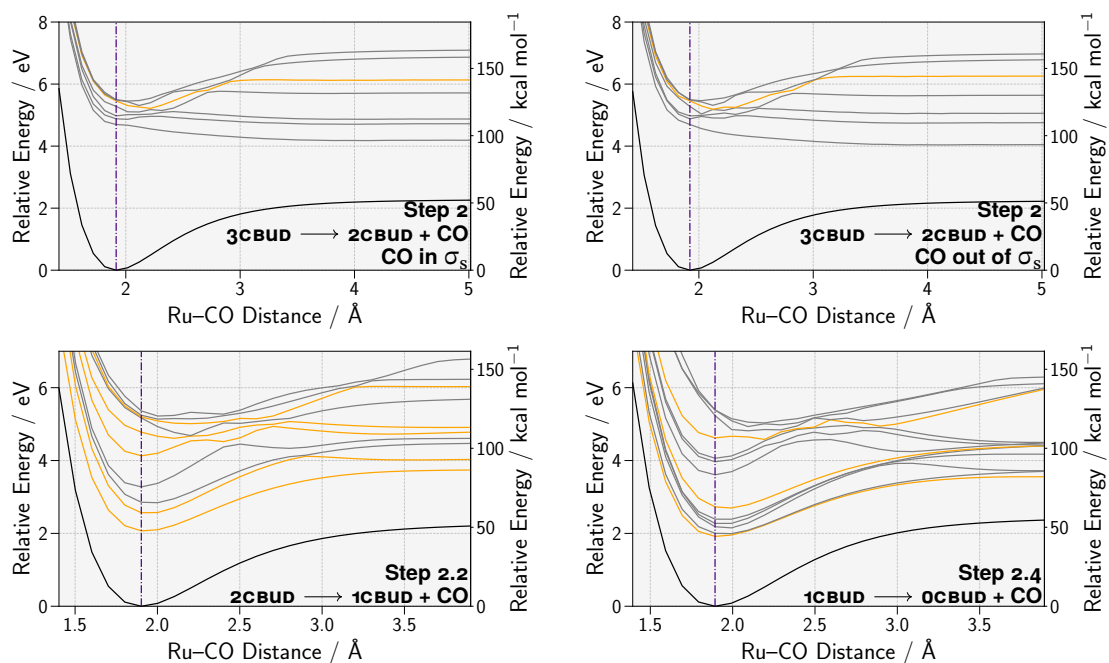


FIGURE A.13 – Rigid scans for Ru-CO dissociation in **3CBuD** and its fragments. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PES. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-svp, def2-TZVP(Ru) + ECP.

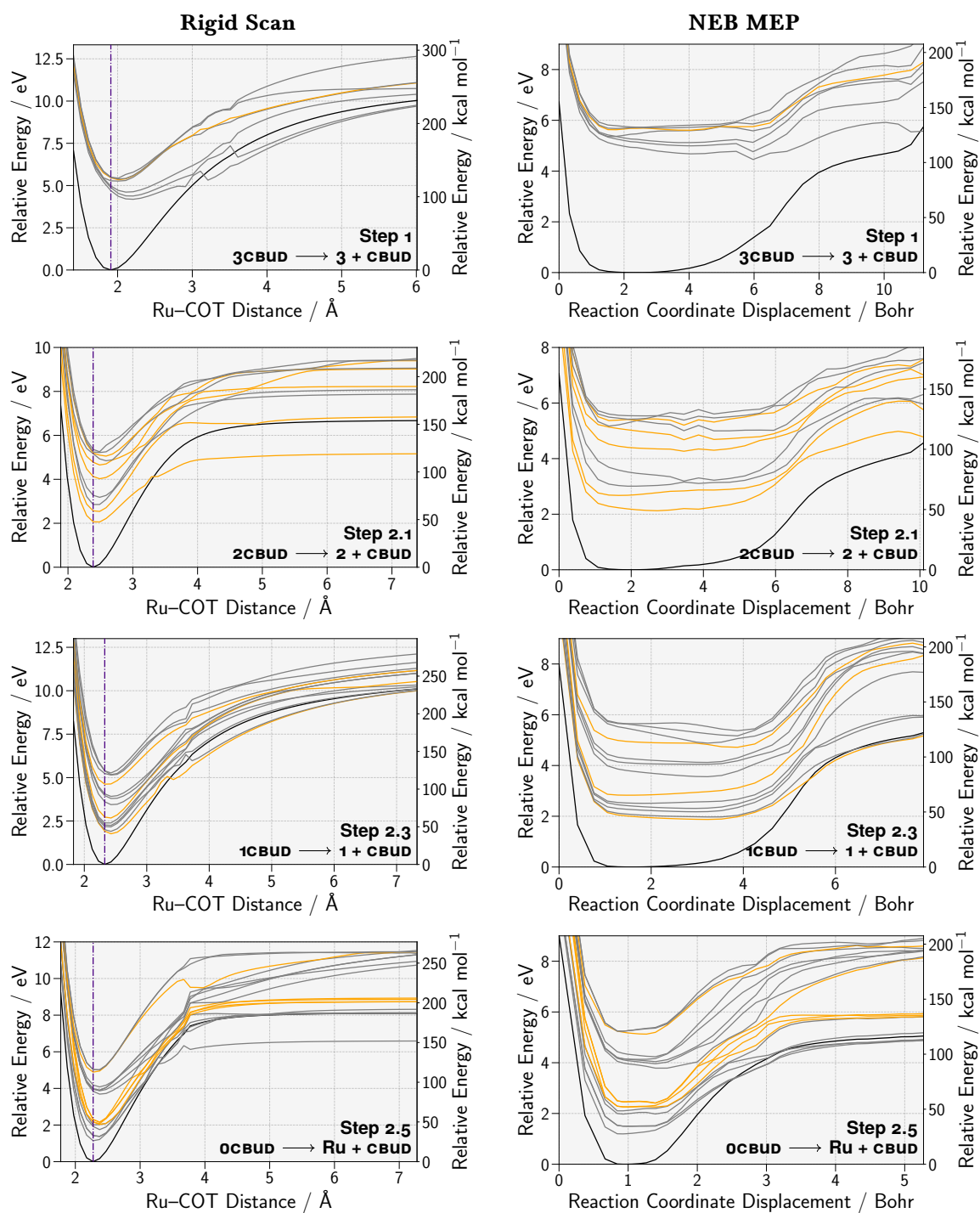


FIGURE A.14 – Rigid scans and NEB MEPs for Ru-CBUD dissociation in **3CBUD** and its fragments. Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP. See Figure A.9 for a schematic visualisation of the NEB MEPs.

A.2.6 $\text{Ru}(\text{CO})_n$

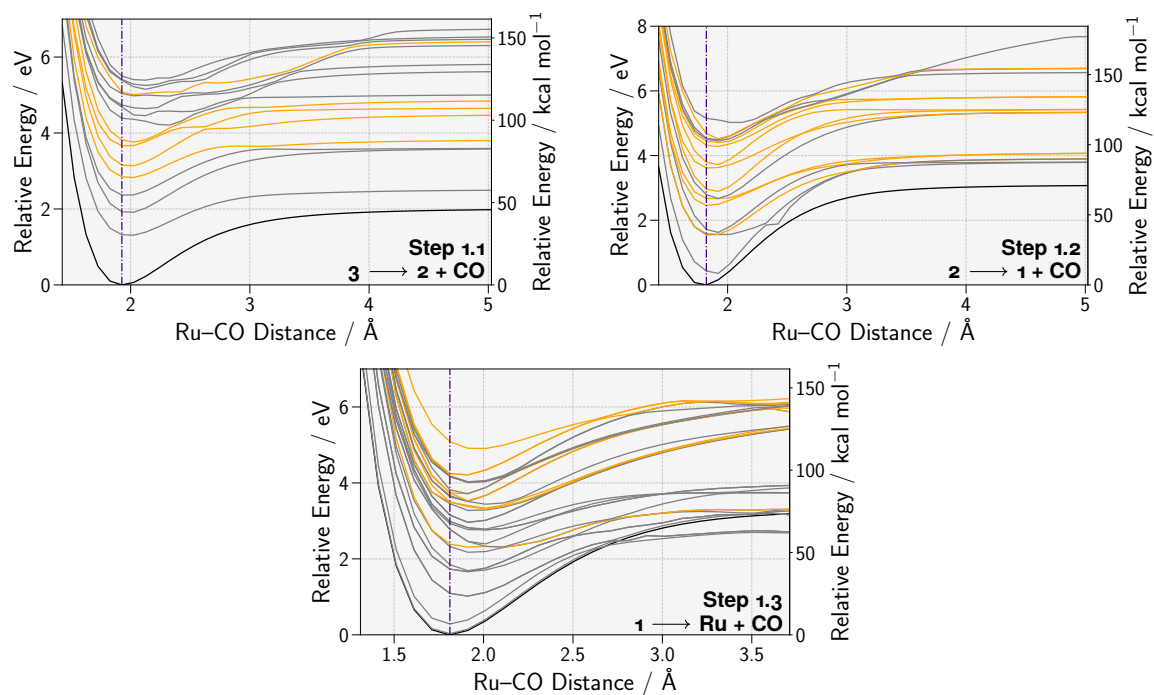
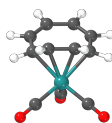


FIGURE A.15 – Rigid scans for Ru–CO dissociation in $\text{Ru}(\text{CO})_n$ ($n = 3, 2, 1$). Purple vertical lines indicate vertical excitation from the GS equilibrium geometry. Black curves are the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ $\omega\text{B97X-D3}/\text{def2-SVP, def2-TZVP}(\text{Ru}) + \text{ECP}$.

A.3 CARTESIAN COORDINATES FOR EQUILIBRIUM GEOMETRIES IN Å

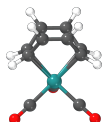
A.3.1 RUTHENIUM COMPLEXES



3COT | η^4 edge | C_s | Singlet

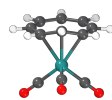
This is the ground state

Ru	0.00000	0.00000	0.00000
C	-1.60967	0.08198	1.57528
C	-0.50317	-0.74935	1.98954
C	0.84238	-0.32439	1.98949
C	1.27047	0.99177	1.57530
C	0.95402	2.32960	2.08679
C	-0.16918	2.92506	2.54745
C	-1.54174	2.49188	2.54647
C	-2.11904	1.35938	2.08547
H	-2.46191	-0.55295	1.31056
H	-0.68523	-1.81587	2.15185
H	1.60403	-1.09288	2.15154
H	2.33276	0.96167	1.31038
H	1.83596	2.97936	2.07741
H	-0.02965	3.95148	2.90025
H	-2.24569	3.25236	2.89801
H	-3.21417	1.38530	2.07438
C	-1.07238	-1.25097	-0.98558
O	-1.70134	-2.00128	-1.57409
C	-0.49631	1.57133	-0.97966
C	1.59631	-0.40818	-0.98579
O	2.54173	-0.66138	-1.57474
O	-0.80341	2.54423	-1.48854



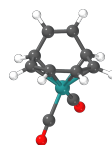
3COT | η^4 center | C_s | Singlet

Ru	0.00000	0.00000	0.00000
C	0.80466	-1.37361	1.58626
C	1.56268	-0.17159	1.61631
C	-0.78594	1.36101	1.61869
C	-1.58140	0.18418	1.58873
C	-1.38581	-0.90461	2.59405
C	-0.26937	-1.63340	2.59295
C	1.35291	0.85588	2.67882
C	0.24045	1.58167	2.68003
H	-2.15907	-1.04882	3.35540
H	-0.08941	-2.39994	3.35349
H	1.27924	-2.25598	1.14540
H	2.57284	-0.20949	1.19580
H	2.10219	0.93660	3.47324
H	0.01337	2.29913	3.47546
H	-1.22636	2.27062	1.19762
H	-2.57999	0.26348	1.14751
C	-0.67692	1.37701	-1.12521
C	1.53006	-0.07591	-1.12770
C	-1.00576	-1.53122	-0.65873
O	-1.12486	2.19942	-1.78500
O	-1.59798	-2.43451	-1.02543
O	2.46169	-0.16051	-1.78889



3COT | η^3 | C_s | Triplet

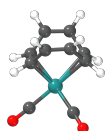
Ru	0.00000	0.00000	0.00000
C	1.94762	-1.96144	-1.44158
C	1.09087	-0.85006	-1.84306
C	1.25604	0.55773	-1.76701
C	1.72793	1.35763	-0.69345
C	2.86393	1.21384	0.21157
C	3.69310	0.17401	0.55432
C	3.77961	-1.19422	0.19940
C	3.04177	-2.08255	-0.62043
H	1.62350	-2.90370	-1.89371
H	0.43000	-1.14015	-2.66521
H	0.66750	1.11142	-2.50416
H	1.45408	2.40961	-0.81670
H	3.08152	2.14882	0.73674
H	4.45828	0.46256	1.28188
H	4.60796	-1.69801	0.70782
H	3.42838	-3.10559	-0.57556
C	-0.80928	-1.66501	0.47631
O	-1.29927	-2.66184	0.74908
C	-0.10498	0.77104	1.74605
C	-1.62141	0.82088	-0.67602
O	-2.63677	1.26337	-0.96181
O	-0.17002	1.24458	2.78513



2COT | η^6 | C_1 | Singlet

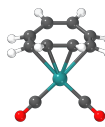
This is the ground state

Ru	0.00000	0.00000	0.00000
C	0.59714	-1.33656	-1.25440
O	0.92728	-2.08393	-2.05865
C	-0.49757	1.03518	-1.47102
O	-0.80703	1.66072	-2.38508
C	0.50851	-1.16741	1.87050
C	1.37317	-0.02529	1.81422
C	1.09074	1.30306	1.40236
C	-0.24667	1.78240	1.25540
C	-1.30953	1.64833	2.28893
C	-2.14137	0.61902	2.20670
C	-1.87413	-0.47720	1.23497
C	-0.85162	-1.41557	1.49899
H	1.08846	-2.09305	1.93316
H	2.43207	-0.27922	1.91172
H	1.95329	1.91711	1.12767
H	-0.30617	2.73386	0.71140
H	-1.40485	2.41757	3.06294
H	-2.97825	0.47941	2.89992
H	-2.75722	-0.90772	0.75207
H	-1.03151	-2.45912	1.22293



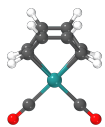
2COT | η^4 center | C_1 | Singlet

Ru	0.00000	0.00000	0.00000
C	0.92556	-1.32422	1.46168
C	1.59296	-0.04714	1.41417
C	-0.95939	1.30539	1.77513
C	-1.55913	0.06597	1.74292
C	-1.19155	-1.04194	2.67168
C	-0.03355	-1.69064	2.53613
C	1.38569	1.00032	2.44819
C	0.21263	1.61972	2.62416
H	-1.89952	-1.28154	3.47159
H	0.22696	-2.50215	3.22458
H	1.48004	-2.16798	1.03470
H	2.59421	-0.03267	0.96949
H	2.24507	1.27665	3.06842
H	0.10009	2.40946	3.37295
H	-1.47316	2.15076	1.30578
H	-2.51382	-0.01898	1.20667
C	-0.35857	1.56583	-1.02829
C	1.11923	-0.64056	-1.34519
O	-0.45760	2.56127	-1.59390
O	1.82658	-1.05542	-2.14710



2COT | η^4 edge | C_s | Triplet

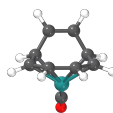
Ru	0.00000	0.00000	0.00000
C	-1.69949	-0.03128	1.66064
C	-0.48989	-0.72622	2.04746
C	0.83391	-0.26816	2.04740
C	1.35547	1.02566	1.66046
C	0.90753	2.34292	1.75872
C	-0.30385	2.96663	2.19232
C	-1.59390	2.52029	2.19183
C	-2.16075	1.28136	1.75773
H	-2.49639	-0.73492	1.40243
H	-0.61873	-1.79009	2.26095
H	1.59269	-1.02498	2.26074
H	2.41684	0.96481	1.40238
H	1.67996	3.06766	1.47941
H	-0.17574	4.01982	2.46034
H	-2.34566	3.26908	2.45949
H	-3.21563	1.37411	1.47748
C	-1.00151	-1.17553	-1.05777
O	-1.57612	-1.95754	-1.67078
C	1.51384	-0.30637	-1.05732
O	2.44887	-0.56655	-1.67014



2COT | η^4 center | C_{2v} | Triplet

Ru	0.00000	0.00000	0.00000
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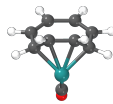
C	-1.36021	-0.91424	2.57449
C	-0.23054	-1.62250	2.57457
C	0.82990	-1.35846	1.55853
C	1.58443	-0.15526	1.55867
C	1.36008	0.91428	2.57465
C	0.23042	1.62256	2.57449
C	-0.82987	1.35847	1.55834
C	-1.58446	0.15526	1.55846
H	-2.13368	-1.07671	3.33274
H	-0.03980	-2.38942	3.33287
H	1.29130	-2.24153	1.10329
H	2.58025	-0.18586	1.10334
H	2.13340	1.07665	3.33305
H	0.03958	2.38951	3.33275
H	-1.29124	2.24154	1.10310
H	-2.58033	0.18596	1.10322
C	-1.15683	0.72524	-1.34175
C	1.15692	-0.72503	-1.34182
O	-1.86959	1.17205	-2.12317
O	1.86977	-1.17154	-2.12334



1COT | η^6 | C_s | Singlet

This is the ground state

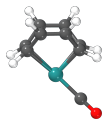
Ru	0.00000	0.00000	0.00000
C	-0.60010	1.43780	1.42103
C	-1.73281	0.57585	1.21311
C	0.82321	-1.63030	1.21299
C	1.50970	-0.38335	1.42091
C	-1.67950	-0.84406	1.28374
C	-0.58914	-1.78524	1.28384
C	1.27361	0.45845	2.62861
C	0.26739	1.32725	2.62858
H	-0.78299	2.47407	1.10934
H	-2.68824	0.99510	0.88342
H	1.37791	-2.51427	0.88407
H	2.56157	-0.41221	1.10908
H	-2.62796	-1.33010	1.03701
H	-0.93132	-2.79461	1.03739
H	1.94524	0.34271	3.48555
H	0.05506	1.97498	3.48543
C	0.95414	1.10418	-1.09088
O	1.53219	1.77367	-1.83922



1COT | η^4 edge | C_s | Singlet

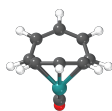
Ru	0.00000	0.00000	0.00000
C	-1.56020	0.03194	1.36101
C	-0.48407	-0.73396	1.99380
C	0.83289	-0.28173	1.99381
C	1.21137	0.98375	1.36101
C	0.90890	2.34631	1.84672
C	-0.23357	2.91467	2.28671
C	-1.60641	2.44329	2.28652
C	-2.15864	1.29296	1.84647
H	-2.36826	-0.65028	1.04895

H	-0.65664	-1.78105	2.27038
H	1.61235	-1.00188	2.27038
H	2.26807	0.94194	1.04886
H	1.77958	3.01115	1.83021
H	-0.13240	3.95392	2.61505
H	-2.32475	3.20120	2.61461
H	-3.25408	1.28271	1.82963
C	-0.47530	1.38394	-1.16243
O	-0.80323	2.33815	-1.71605



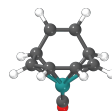
1COT | η^4 center | C_1 | Singlet

Ru	0.00000	0.00000	0.00000
C	0.85158	1.31760	2.58528
C	-0.45216	1.58071	2.48264
C	-1.23271	0.98308	1.36775
C	-1.53880	-0.43999	1.30085
C	-1.02368	-1.41564	2.29887
C	0.29032	-1.65808	2.42616
C	1.28128	-0.96301	1.56633
C	1.49023	0.41992	1.58675
H	1.46986	1.73247	3.38764
H	-0.96065	2.23382	3.19951
H	-2.00132	1.65395	0.96391
H	-2.51006	-0.71055	0.86702
H	-1.74532	-1.96649	2.91153
H	0.65032	-2.40978	3.13599
H	2.03678	-1.58765	1.06909
H	2.39402	0.79344	1.08279
C	-1.09152	0.71494	-1.34418
O	-1.75565	1.21474	-2.13963



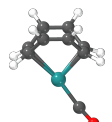
1COT | η^5 edge | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.29419	-0.37325	1.72057
C	-0.03299	-0.96416	2.00221
C	1.26564	-0.46079	1.72065
C	1.62517	0.84457	1.23612
C	1.32122	2.15278	1.80582
C	0.09313	2.72287	2.11014
C	-1.17104	2.23799	1.80587
C	-1.56363	0.95363	1.23605
H	-2.12915	-1.08218	1.69612
H	-0.06954	-2.03252	2.23472
H	2.05022	-1.22511	1.69626
H	2.63954	0.82880	0.81918
H	2.19606	2.79643	1.94540
H	0.12750	3.72794	2.54068
H	-1.99988	2.93984	1.94558
H	-2.57670	1.00724	0.81908
C	0.04323	1.26595	-1.38246
O	0.07179	2.10310	-2.17223



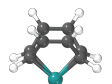
1COT | η^6 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	0.54201	0.79283	-1.67573
O	0.96104	1.40542	-2.55456
C	-1.21512	-0.52583	1.86029
C	-0.04737	-1.32316	1.86028
C	1.28622	-1.03510	1.40289
C	1.86232	0.24087	1.19175
C	1.73385	1.36355	2.15792
C	0.63862	2.11139	2.15778
C	-0.45368	1.82216	1.19152
C	-1.43237	0.82106	1.40281
H	-2.13261	-1.10652	1.99708
H	-0.25416	-2.38910	1.99708
H	1.84520	-1.92110	1.08127
H	2.82193	0.20323	0.66265
H	2.55244	1.53027	2.86680
H	0.49580	2.93458	2.86654
H	-0.83814	2.70217	0.66236
H	-2.46108	1.01906	1.08120



1COT | η^4 center | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.49550	-0.70671	2.55123
C	-0.52216	-1.62387	2.45403
C	0.59684	-1.52346	1.48684
C	1.55951	-0.49181	1.48798
C	1.58282	0.62642	2.46146
C	0.60165	1.53442	2.55953
C	-0.60661	1.51013	1.69939
C	-1.54974	0.50515	1.69802
H	-2.32697	-0.86233	3.24624
H	-0.57321	-2.52483	3.07488
H	0.89401	-2.47032	1.02293
H	2.52494	-0.72286	1.02465
H	2.47480	0.73200	3.08835
H	0.69479	2.36930	3.26164
H	-0.87626	2.45435	1.21060
H	-2.50906	0.71451	1.20920
C	0.71874	-0.67520	-1.61276
O	1.23050	-1.15201	-2.52876

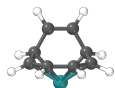


oCOT | η^4 center | C_{2v} | Singlet

This is the ground state

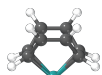
Ru	0.00000	0.00000	0.00000
C	-2.66585	-1.15267	0.31057
C	-1.89940	-1.94496	1.06829
C	-0.46352	-1.57192	1.21543
C	-0.04072	-0.41482	1.99753
C	-1.01771	0.46645	2.69789

C	-1.78416	1.25875	1.94015
C	-1.59221	1.18900	0.46369
C	-2.01509	0.03198	-0.31849
H	-3.73133	-1.34744	0.15093
H	-2.29386	-2.83339	1.57204
H	0.25560	-2.40768	1.16994
H	0.95614	-0.49149	2.46451
H	-1.09407	0.44896	3.78992
H	-2.53113	1.93449	2.36921
H	-1.60508	2.15610	-0.06755
H	-2.30590	0.24020	-1.36241



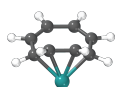
oCOT | η^6 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.20645	-0.52574	1.84974
C	-0.02280	-1.31583	1.84974
C	1.29797	-1.03140	1.35582
C	1.85178	0.25999	1.07463
C	1.73781	1.40646	2.02038
C	0.63236	2.14436	2.02038
C	-0.47014	1.80988	1.07463
C	-1.45035	0.80310	1.35582
H	-2.11403	-1.11228	2.03126
H	-0.21638	-2.37897	2.03125
H	1.88425	-1.92232	1.09790
H	2.81823	0.20367	0.55462
H	2.56869	1.60528	2.70680
H	0.49729	2.98794	2.70680
H	-0.89284	2.68081	0.55462
H	-2.49801	1.00284	1.09791



oCOT | η^4 center | C_s | Triplet

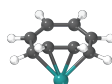
Ru	0.00000	0.00000	0.00000
C	-1.38686	-0.91446	2.40254
C	-0.26322	-1.64022	2.40255
C	0.74148	-1.34749	1.34072
C	1.53314	-0.12169	1.34109
C	1.38675	0.91428	2.40269
C	0.26309	1.64006	2.40269
C	-0.74142	1.34746	1.34109
C	-1.53320	0.12173	1.34072
H	-2.17657	-1.05787	3.14716
H	-0.06918	-2.41905	3.14716
H	1.22211	-2.22766	0.88031
H	2.53290	-0.19781	0.88027
H	2.17627	1.05806	3.14745
H	0.06947	2.41886	3.14744
H	-1.22196	2.22745	0.88027
H	-2.53316	0.19787	0.88031



oCOT | η^4 edge | C_s | Singlet

Ru	0.00000	0.00000	0.00000
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C	-1.58571	0.08539	1.33595
C	-0.50887	-0.75295	1.82766
C	0.85077	-0.31968	1.82759
C	1.24382	0.98724	1.33599
C	0.95959	2.33134	1.87328
C	-0.16625	2.91161	2.34081
C	-1.54929	2.47105	2.34020
C	-2.13167	1.34639	1.87245
H	-2.42106	-0.55420	1.00256
H	-0.68220	-1.82151	2.00586
H	1.61041	-1.09091	2.00579
H	2.29518	0.94907	1.00249
H	1.84226	2.98182	1.87621
H	-0.03788	3.93535	2.70743
H	-2.24647	3.23199	2.70604
H	-3.22794	1.36652	1.87437



oCOT | η^4 edge | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.59167	-0.04033	1.38615
C	-0.46689	-0.73258	2.02041
C	0.83365	-0.24430	2.02033
C	1.22492	1.01721	1.38621
C	0.83774	2.38031	1.69218
C	-0.33968	2.93586	2.11680
C	-1.67646	2.43399	2.11659
C	-2.19726	1.24083	1.69188
H	-2.36696	-0.76390	1.08996
H	-0.61009	-1.77767	2.31825
H	1.62928	-0.93691	2.31815
H	2.28484	0.98269	1.09002
H	1.65167	3.09787	1.54118
H	-0.27605	4.00438	2.34667
H	-2.42762	3.19664	2.34625
H	-3.28228	1.24546	1.54060



3BuD | η^4 | C_s | Singlet

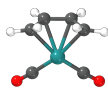
This is the ground state

Ru	0.00000	-0.00000	0.00000
C	-1.38792	0.57062	1.61071
C	-0.04966	0.93221	1.98274
C	0.92956	-0.09083	1.98203
C	0.50803	-1.41200	1.61046
H	-0.40997	-1.82232	2.04035
H	1.29275	-2.15833	1.46234
H	1.98103	0.16505	2.13479
H	0.25161	1.97162	2.13564
H	-2.09748	1.38889	1.46265
H	-1.84096	-0.32690	2.04094
C	-1.21805	-1.17671	-0.90181
C	-0.32955	1.59805	-1.01524
C	1.58419	-0.39545	-1.01217
O	-1.95610	-1.89881	-1.38868
O	-0.52548	2.54832	-1.61906
O	2.52259	-0.63732	-1.61783



3BuD | η^2 | C_1 | Triplet

Ru	0.00000	0.00000	0.00000
C	0.16741	0.30825	1.87984
C	-0.78928	1.71225	-0.40565
C	-1.61079	-1.03552	-0.00859
O	0.18538	0.45187	3.01557
O	-1.28334	2.72542	-0.60456
O	-2.57613	-1.64488	0.08028
C	3.32750	0.57311	0.50525
C	2.63151	0.28579	-0.63949
C	1.84195	-0.89475	-0.89586
C	1.36074	-1.78843	0.08050
H	1.83187	-1.83963	1.06530
H	0.90581	-2.72249	-0.25510
H	1.57959	-1.08360	-1.94337
H	2.73439	0.97232	-1.48561
H	3.90243	1.49642	0.58972
H	3.31725	-0.09383	1.37083



2BuD | η^4 | C_s | Singlet

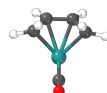
This is the ground state

Ru	0.00000	-0.00000	0.00000
C	-1.40893	0.58748	1.62756
C	-0.07710	0.92899	1.94134
C	0.92722	-0.09591	1.94139
C	0.55880	-1.42055	1.62769
H	-0.39434	-1.83693	1.96909
H	1.35563	-2.15600	1.49626
H	1.97385	0.19652	2.05702
H	0.23647	1.96947	2.05699
H	-2.12805	1.39906	1.49607
H	-1.84462	-0.35695	1.96908
C	-0.38907	1.52698	-1.05900
C	1.51905	-0.41982	-1.05871
O	-0.57752	2.49920	-1.63751
O	2.48676	-0.62779	-1.63810



2BuD | η^4 | C_s | Triplet

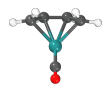
Ru	0.00000	0.00000	0.00000
C	-1.29213	-1.31047	-0.48025
C	1.09789	-1.24238	0.93205
O	-2.10280	-2.07567	-0.75021
O	1.75710	-1.96548	1.53052
C	-1.36765	1.70544	-0.55107
C	-0.13951	1.81704	-1.25430
C	1.08864	1.85202	-0.52837
C	1.06875	1.77490	0.88901
H	0.29602	2.28954	1.46846
H	2.02205	1.65245	1.40722
H	2.03148	1.78995	-1.07866
H	-0.10887	1.72897	-2.34376
H	-2.27501	1.52996	-1.13265
H	-1.52482	2.23762	0.39221



1BuD | η^4 | C_s | Singlet

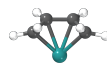
This is the ground state

Ru	0.00000	0.00000	0.00000
C	1.78440	0.00016	0.54905
O	2.79740	-0.00110	1.09888
C	-0.78562	-1.38074	1.32378
C	-1.92640	-0.70090	0.73396
C	-1.92694	0.69871	0.73461
C	-0.78662	1.37871	1.32522
H	-0.50828	1.15868	2.36427
H	-0.69357	2.44779	1.09287
H	-2.66670	1.23335	0.12879
H	-2.66570	-1.23549	0.12752
H	-0.69189	-2.44953	1.09035
H	-0.50726	-1.16154	2.36298



1BuD | η^4 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-0.10689	-1.44260	1.24574
O	-0.18095	-2.29589	2.01157
C	-1.82079	1.14863	-0.32658
C	-0.79009	1.70356	-1.13605
C	0.49933	2.04055	-0.63508
C	0.88150	1.85520	0.72327
H	0.19275	2.10482	1.54016
H	1.93415	1.99574	0.98232
H	1.27851	2.23754	-1.37897
H	-0.89932	1.66838	-2.22512
H	-2.72006	0.77845	-0.82579
H	-2.00740	1.52945	0.68543



oBuD | η^4 | C_s | Singlet

This is the ground state

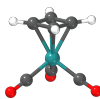
Ru	0.00000	-0.00000	0.00000
C	-1.38744	0.59496	1.40744
C	-0.04770	0.93692	1.82014
C	0.93181	-0.10863	1.82017
C	0.50333	-1.42325	1.40746
H	-0.36723	-1.90540	1.87480
H	1.30757	-2.14006	1.18876
H	1.98585	0.15188	1.96941
H	0.28093	1.97175	1.96942
H	-2.05034	1.44416	1.18869
H	-1.92529	-0.24231	1.87484



oBuD | η^4 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	1.34452	1.49876	0.88662
C	1.97873	0.72839	-0.11663
C	1.98394	-0.71880	-0.12785
C	1.35687	-1.51025	0.86248

H	1.37841	-1.21367	1.91938
H	1.32028	-2.59212	0.70587
H	2.34746	-1.19890	-1.04389
H	2.34017	1.22589	-1.02411
H	1.30110	2.58292	0.74787
H	1.36980	1.18615	1.93890



3CBuD | η^4 | C_s | Singlet

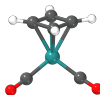
This is the ground state

Ru	0.00000	-0.00000	0.00000
C	-1.02652	-0.03732	1.91411
C	-0.04513	1.01913	1.94421
C	1.02753	0.05287	1.90650
C	0.04413	-1.03468	1.87229
H	-0.09324	2.10277	2.03608
H	-2.10594	-0.07725	2.04271
H	2.10520	0.10703	2.04269
H	0.09014	-2.10588	2.05130
C	-1.42120	-0.84372	-0.96880
C	-0.01635	1.63061	-1.01630
C	1.44027	-0.81806	-0.96067
O	-2.28452	-1.37559	-1.49643
O	-0.02437	2.62215	-1.58640
O	2.31722	-1.33286	-1.48268



3CBuD | η^4 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.05867	-0.35810	1.56785
C	-1.62205	-1.00551	-1.08886
C	0.92536	-1.68009	-0.16757
O	-1.67235	-0.53795	2.51625
O	-2.20697	-1.99549	-1.00922
O	1.50951	-2.65847	-0.26728
C	-0.69397	1.86897	-0.98077
C	0.28263	1.21793	-1.83685
C	1.32111	1.48447	-0.86806
C	0.33390	2.14269	-0.00288
H	0.26458	0.79846	-2.84002
H	-1.74346	2.13611	-1.08009
H	2.40621	1.40471	-0.87692
H	0.38304	2.75389	0.89594



2CBuD | η^4 | C_s | Singlet

This is the ground state

Ru	0.00000	-0.00000	0.00000
C	-0.88781	0.53442	1.89259
C	0.54452	0.87534	1.77099
C	0.87165	-0.56014	1.89323
C	-0.52836	-0.84962	1.99464
H	1.11432	1.79127	1.91923
H	-1.80306	1.10191	2.03970
H	1.78543	-1.13045	2.03871

H	-1.10272	-1.77329	2.08510
C	-0.81826	1.40780	-0.98318
C	1.62417	-0.12005	-0.98281
O	-1.26175	2.35239	-1.45925
O	2.66762	-0.10567	-1.45886



2CBuD | η^4 | C_{2v} | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.14955	-1.38239	-0.69472
C	-1.34403	1.31931	0.41018
O	-1.81408	-2.21768	-1.11100
O	-2.12629	2.11767	0.66182
C	1.87599	-0.90553	0.60474
C	1.77903	0.44710	1.15781
C	1.91700	1.00059	-0.17162
C	2.01401	-0.35202	-0.72466
H	1.77877	0.87123	2.15970
H	1.97779	-1.90376	1.02523
H	2.06179	2.00504	-0.56375
H	2.26013	-0.77001	-1.69851



1CBuD | η^4 | C_s | Singlet

This is the ground state

Ru	0.00000	-0.00000	0.00000
C	-0.88257	0.53145	1.78515
C	0.53090	0.88030	1.82207
C	0.88141	-0.53075	1.87950
C	-0.52974	-0.88101	1.82192
H	1.07863	1.81445	1.93911
H	-1.81125	1.09062	1.88261
H	1.80224	-1.08529	2.05031
H	-1.09910	-1.80209	1.93925
C	-1.37911	0.82988	-0.99659
O	-2.31084	1.39053	-1.37914



1CBuD | η^4 | C_s | Triplet

Ru	0.00000	0.00000	0.00000
C	-0.58464	-1.26738	1.28899
O	-0.90063	-2.01033	2.11056
C	0.63262	2.07433	-0.40536
C	1.68362	1.16238	-0.82388
C	1.88390	0.73897	0.54508
C	0.80897	1.67221	0.97277
H	2.18455	0.95779	-1.76865
H	0.02785	2.82534	-0.91103
H	2.65893	0.18902	1.07514
H	0.49220	2.06618	1.93634



oCBuD | η^4 | C_{4v} | Singlet

This is the ground state

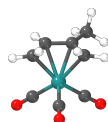
Ru	0.00000	-0.00000	0.00000
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C	-0.86824	0.56130	1.77429
C	0.56127	0.86806	1.77444
C	0.86816	-0.56143	1.77424
C	-0.56120	-0.86793	1.77486
H	1.14761	1.77486	1.92318
H	-1.77477	1.14755	1.92456
H	1.77476	-1.14755	1.92456
H	-1.14760	-1.77485	1.92300



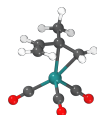
oCBuD | η^4 | C_{2v} | Triplet

Ru	0.00000	0.00000	0.00000
C	1.84715	-0.74289	-0.72024
C	1.84772	-0.74990	0.71343
C	1.84714	0.74290	0.72024
C	1.84772	0.74991	-0.71343
H	2.00228	-1.51439	1.47316
H	2.00312	-1.49995	-1.48710
H	2.00312	1.49996	1.48710
H	2.00226	1.51440	-1.47316



3MBuD | η^4 | C_1 | Singlet
This is the ground state

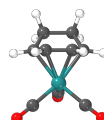
Ru	0.00000	-0.00000	0.00000
C	-1.40312	0.52698	1.59955
C	-0.07608	0.92513	1.98069
C	0.94465	-0.06225	1.99410
C	0.53455	-1.38986	1.61474
H	-0.37659	-1.81648	2.04261
H	1.33393	-2.12381	1.47475
H	0.19188	1.97312	2.14310
H	-2.13097	1.32808	1.44604
H	-1.83745	-0.37711	2.03561
C	2.37313	0.28483	2.31288
H	2.59216	1.34142	2.10370
H	3.07089	-0.33905	1.73734
H	2.56693	0.09654	3.38086
C	-1.17389	-1.21526	-0.91088
C	-0.38639	1.58890	-1.00591
C	1.61293	-0.34172	-0.98496
O	-1.89011	-1.95809	-1.40005
O	-0.63261	2.54269	-1.58592
O	2.58552	-0.56335	-1.54395



3MBuD | η^2 | C_1 | Triplet

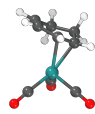
Ru	0.00000	0.00000	0.00000
C	-0.45378	-1.51422	-1.07813
C	-0.88551	-0.62422	1.59364
C	-1.35152	1.21860	-0.59245
O	-0.79342	-2.37571	-1.75150
O	-1.44044	-1.01326	2.51669

O	-2.18989	1.88528	-0.99856
C	2.80109	-1.79540	-0.17468
C	2.51587	-0.60875	0.46227
C	2.13463	0.64508	-0.15195
C	1.56135	0.69926	-1.44442
H	1.74803	-0.09975	-2.16567
H	1.40045	1.68263	-1.89276
H	2.71285	-0.55746	1.53871
H	3.10003	-2.67321	0.39981
H	2.70940	-1.90896	-1.25726
C	2.36388	1.91622	0.63110
H	2.23103	1.76265	1.71219
H	1.68844	2.72025	0.30609
H	3.39873	2.26441	0.46950



3CHD | η^4 | C_s | Singlet
This is the ground state

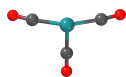
Ru	0.00000	-0.00000	0.00000
C	-1.32297	-0.59953	1.65448
C	-0.69093	0.65400	1.97064
C	0.72527	0.61577	1.97057
C	1.28862	-0.67024	1.65440
C	0.71703	-1.91339	2.31947
C	-0.81941	-1.87222	2.31870
H	-2.40612	-0.56123	1.50061
H	-1.23641	1.59162	2.09767
H	1.32063	1.52248	2.09787
H	2.37227	-0.69048	1.50056
H	1.10787	-1.98589	3.34906
H	1.08450	-2.80421	1.78923
H	-1.21473	-1.92487	3.34781
H	-1.23393	-2.74128	1.78697
C	-0.04683	-1.68955	-0.90048
C	-1.37383	0.89430	-1.00579
C	1.42124	0.81657	-1.00587
O	-0.07574	-2.72909	-1.37449
O	-2.21562	1.41177	-1.58083
O	2.29070	1.28617	-1.58080



3CHD | η^2 | C_1 | Triplet

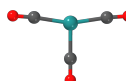
Ru	0.00000	0.00000	0.00000
C	-0.27256	-0.37952	1.84170
C	1.21313	-1.42376	-0.38638
C	1.30428	1.39888	0.27889
O	-0.35686	-0.68388	2.94493
O	1.94386	-2.29583	-0.52387
O	2.10627	2.18648	0.49756
C	-1.78911	0.03867	-1.36575
C	-2.54061	1.18672	-0.89818
C	-3.34817	1.11295	0.19275
C	-3.44107	-0.12276	1.03811
H	-1.29688	0.09619	-2.34287
H	-2.46026	2.12017	-1.45983
H	-3.89440	2.00165	0.52005

H	-4.47314	-0.25852	1.39794
H	-2.84397	0.05412	1.95157
C	-2.96251	-1.39852	0.32869
C	-1.83466	-1.17852	-0.66343
H	-3.80343	-1.82557	-0.24832
H	-2.68762	-2.16081	1.07216
H	-1.50252	-2.07765	-1.18952



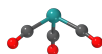
3 | C_s | Singlet
This is the ground state

Ru	0.00000	0.00000	0.00000
C	-1.50997	0.36272	1.13998
C	-1.05090	-1.04904	-1.03420
C	1.49890	-1.14973	-0.38084
O	-2.36522	0.41402	1.89801
O	-1.71764	-1.69230	-1.71390
O	2.32034	-1.94080	-0.47074



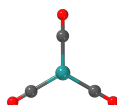
3 | C_{2v} | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.41612	0.90840	1.02373
C	-1.06430	-0.70535	-1.40288
C	1.75334	-0.68465	-0.57910
O	-2.29700	1.40570	1.55411
O	-1.70687	-1.13187	-2.24958
O	2.72751	-1.11976	-0.98686



3 | C_{3v} | Triplet

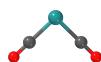
Ru	0.00000	0.00000	0.00000
C	-0.56209	-0.30001	1.80366
C	-1.32888	-1.02112	-0.92193
C	1.46219	-1.23018	-0.08659
O	-0.89888	-0.64070	2.84414
O	-2.08440	-1.75587	-1.37073
O	2.23157	-2.07870	-0.07869



3 | D_{3h} | Singlet

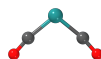
Ru	0.00000	0.00000	0.00000
C	-1.06950	1.03122	1.29215
C	-0.82101	-0.63977	-1.67125
C	1.89214	-0.39052	0.37861
O	-1.69013	1.63146	2.04320

O	-1.29800	-1.01118	-2.64286
O	2.99247	-0.61620	0.59740



2 | C_{2v} | Singlet
This is the ground state

Ru	0.00000	0.00000	0.00000
C	-0.99230	-1.32560	-0.97530
C	1.38883	-1.25726	0.42541
O	-1.58236	-2.11396	-1.55523
O	2.21255	-2.00505	0.68662



2 | C_{2v} | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.08101	-1.18334	-0.98298
C	1.43194	-1.11135	0.49962
O	-1.61210	-2.03381	-1.54644
O	2.21753	-1.92387	0.71298



2 | D_{∞h} | Triplet

Ru	0.00000	0.00000	0.00000
C	-1.44921	-0.75897	-1.06991
C	1.44902	0.75907	1.07011
O	-2.29355	-1.20107	-1.69333
O	2.29333	1.20154	1.69331



2 | D_{∞h} | Singlet

Ru	0.00000	0.00000	0.00000
C	-1.44958	-0.75908	-1.06984
C	1.44909	0.75923	1.07040
O	-2.29352	-1.20068	-1.69316
O	2.29294	1.20168	1.69324



1 | C_{∞v} | Triplet
This is the ground state

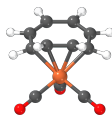
Ru	0.00000	0.00000	0.00000
C	1.30849	-1.18566	0.40558
O	2.14017	-1.93927	0.66337



1 | C_{∞v} | Singlet

Ru	0.00000	0.00000	0.00000
C	1.30849	-1.18566	0.40558
O	2.14017	-1.93927	0.66337

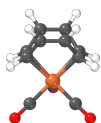
A.3.2 IRON ANALOGUE COMPLEXES



3COT | η^4 edge | C_s | Singlet

This is the ground state

Fe	0.00000	0.00000	0.00000
C	-1.59818	0.07919	1.42985
C	-0.49922	-0.74912	1.84151
C	0.84104	-0.32103	1.84150
C	1.25636	0.99097	1.42986
C	0.94238	2.33305	1.93275
C	-0.18125	2.93477	2.38201
C	-1.55356	2.49646	2.38195
C	-2.12032	1.35480	1.93266
H	-2.44766	-0.55151	1.14448
H	-0.67921	-1.81899	1.98378
H	1.60789	-1.08847	1.98377
H	2.31414	0.96949	1.14447
H	1.82677	2.97933	1.92693
H	-0.04365	3.96348	2.72858
H	-2.26202	3.25495	2.72845
H	-3.21560	1.36878	1.92675
C	-0.99089	-1.19033	-0.91571
O	-1.62603	-1.94193	-1.49407
C	-0.48455	1.51706	-0.82360
C	1.49742	-0.39559	-0.91571
O	2.45069	-0.63961	-1.49410
O	-0.80140	2.50951	-1.28527



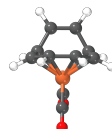
3COT | η^4 center | C_s | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.38710	-0.90571	2.47133
C	-0.27158	-1.63483	2.47008
C	0.78666	-1.35759	1.45748
C	1.54605	-0.16710	1.48684
C	1.36155	0.86676	2.54180
C	0.24924	1.59342	2.54337
C	-0.77348	1.34864	1.48983
C	-1.55923	0.17605	1.46025
H	-2.17260	-1.05278	3.21905
H	-0.09013	-2.41404	3.21684
H	1.24337	-2.23181	0.98197
H	2.55045	-0.21014	1.05266
H	2.12989	0.96762	3.31507
H	0.03415	2.33653	3.31793
H	-1.21545	2.25157	1.05563
H	-2.54324	0.24376	0.98478
C	-0.60050	1.30468	-1.06108
C	1.43261	-0.03879	-1.06501
C	-0.92787	-1.40992	-0.61260
O	-1.00421	2.13092	-1.74346
O	-1.51856	-2.30911	-0.99824
O	2.34970	-0.08448	-1.74913



3COT | η^3 | C_s | Triplet

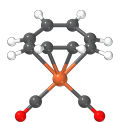
Fe	0.00000	0.00000	0.00000
C	2.16481	-2.15431	-0.56324
C	1.28485	-1.24544	-1.27334
C	1.34970	0.14700	-1.52241
C	1.70468	1.21556	-0.66380
C	2.76698	1.37578	0.31107
C	3.69313	0.52125	0.87020
C	3.93045	-0.87052	0.80828
C	3.26557	-1.98532	0.24934
H	1.90057	-3.20160	-0.73945
H	0.70013	-1.77349	-2.03299
H	0.75209	0.46302	-2.38678
H	1.37505	2.18405	-1.05265
H	2.85821	2.41207	0.65087
H	4.39721	1.03370	1.53342
H	4.80541	-1.16542	1.39636
H	3.72033	-2.93432	0.55062
C	-1.36099	-1.19191	-0.07288
O	-2.18774	-1.97906	-0.12259
C	0.66978	-0.52839	1.67218
C	-0.90948	1.45291	0.58313
O	-1.44179	2.39053	0.96144
O	1.02545	-0.84489	2.70598



2COT | η^6 | C_s | Singlet

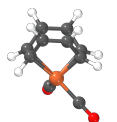
This is the ground state

Fe	0.00000	0.00000	0.00000
C	-0.78490	-1.09319	-1.20628
O	-1.26331	-1.75956	-2.00785
C	0.67360	0.93870	-1.33945
O	1.12662	1.57010	-2.18320
C	-1.22206	-0.48542	1.66352
C	-0.06751	-1.31345	1.66315
C	1.26208	-1.06863	1.20510
C	1.82924	0.21373	1.05286
C	1.72774	1.27279	2.09292
C	0.65081	2.04545	2.09233
C	-0.38476	1.80136	1.05234
C	-1.41698	0.85240	1.20534
H	-2.14504	-1.07054	1.71860
H	-0.32570	-2.37533	1.71822
H	1.80510	-1.95675	0.86924
H	2.76716	0.22007	0.48426
H	2.53196	1.36968	2.83009
H	0.48447	2.83872	2.82900
H	-0.68039	2.69155	0.48385
H	-2.43258	1.08148	0.86991



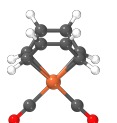
2COT | η^4 edge | C_s | Triplet

Fe	0.00000	0.00000	0.00000
C	-1.05474	-0.98729	-1.08272
O	-1.69042	-1.64660	-1.76934
C	1.43548	-0.16357	-1.08266
O	2.33897	-0.31374	-1.76923
C	-1.71194	-0.00600	1.55737
C	-0.49361	-0.72363	1.90878
C	0.82776	-0.28651	1.90879
C	1.37779	1.01614	1.55748
C	0.94644	2.32279	1.65284
C	-0.26136	2.95099	2.12085
C	-1.55009	2.52466	2.12076
C	-2.14493	1.30013	1.65268
H	-2.50750	-0.69754	1.26318
H	-0.64413	-1.78625	2.11578
H	1.58229	-1.04972	2.11580
H	2.42881	0.93547	1.26332
H	1.71628	3.04707	1.36505
H	-0.11113	3.98733	2.43982
H	-2.28875	3.26696	2.43967
H	-3.19480	1.42242	1.36479



2COT | η^4 center | C_1 | Singlet

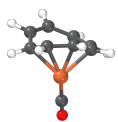
Fe	0.00000	0.00000	0.00000
C	-1.30901	-1.12176	2.21114
C	-0.11323	-1.72385	2.33712
C	1.02313	-1.28683	1.49565
C	1.44636	0.03628	1.51607
C	1.09303	0.99425	2.60458
C	-0.05931	1.64612	2.47641
C	-0.91914	1.27954	1.32386
C	-1.55034	-0.02899	1.23354
H	-2.15755	-1.47608	2.80652
H	0.01991	-2.57218	3.01449
H	1.62852	-2.05124	0.99951
H	2.31568	0.28420	0.88171
H	1.75784	1.09135	3.46844
H	-0.40994	2.37497	3.21488
H	-1.52022	2.10595	0.92539
H	-2.55576	-0.04977	0.79613
C	-0.76828	1.02577	-1.24436
C	-0.25247	-1.54894	-0.87411
O	-1.25092	1.71903	-2.01613
O	-0.56025	-2.53544	-1.37006



2COT | η^4 center | C_{2v} | Triplet

Fe	0.00000	0.00000	0.00000
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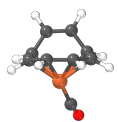
C	-1.36549	-0.92275	2.44434
C	-0.23573	-1.63109	2.44436
C	0.81772	-1.34498	1.43387
C	1.56687	-0.15012	1.43388
C	1.36547	0.92276	2.44436
C	0.23572	1.63111	2.44433
C	-0.81772	1.34499	1.43384
C	-1.56688	0.15012	1.43385
H	-2.15536	-1.10301	3.18143
H	-0.05390	-2.42059	3.18146
H	1.25903	-2.21726	0.93900
H	2.54429	-0.16735	0.93902
H	2.15533	1.10303	3.18147
H	0.05388	2.42062	3.18142
H	-1.25904	2.21726	0.93897
H	-2.54430	0.16736	0.93900
C	-1.08241	0.67844	-1.28671
C	1.08244	-0.67845	-1.28669
O	-1.78558	1.11918	-2.07888
O	1.78560	-1.11920	-2.07886



1COT | η^4 edge | C_1 | Triplet

This is the ground state

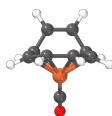
Fe	0.00000	0.00000	0.00000
C	-1.71831	-0.12655	1.58854
C	-0.45146	-0.74488	1.94731
C	0.84127	-0.22571	1.94730
C	1.32850	1.09714	1.58862
C	0.81877	2.38263	1.72396
C	-0.43300	2.92563	2.12743
C	-1.71095	2.41237	2.12748
C	-2.23939	1.15439	1.72407
H	-2.47368	-0.87299	1.32001
H	-0.51954	-1.81676	2.16019
H	1.63184	-0.95272	2.16024
H	2.39031	1.08053	1.32000
H	1.55987	3.15532	1.49092
H	-0.37731	3.99131	2.37095
H	-2.48826	3.14349	2.37104
H	-3.30911	1.19978	1.49117
C	-0.29200	0.72611	-1.66558
O	-0.50287	1.25046	-2.66005



1COT | η^6 | C_1 | Triplet

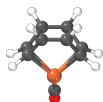
Fe	0.00000	0.00000	0.00000
C	0.47811	0.89016	-1.59526
O	0.83443	1.60515	-2.41635
C	-1.04143	-0.83865	1.65336
C	0.29544	-1.31119	1.64851
C	1.51505	-0.66564	1.25164
C	1.76887	0.71156	1.12453
C	1.30883	1.75173	2.07544
C	0.05944	2.20540	2.06516

C	-0.95102	1.67393	1.11590
C	-1.58690	0.42999	1.24462
H	-1.78270	-1.63956	1.72711
H	0.36602	-2.40128	1.71899
H	2.27753	-1.36119	0.87649
H	2.71577	0.94045	0.61882
H	2.04083	2.13690	2.79822
H	-0.26898	2.97405	2.77253
H	-1.55863	2.43488	0.61216
H	-2.60485	0.34919	0.84684



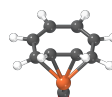
1COT | η^6 | C_s | Singlet

Fe	0.00000	0.00000	0.00000
C	0.39203	0.64171	-1.57373
O	0.64231	1.05116	-2.61902
C	-1.17445	-0.54328	1.65086
C	0.05288	-1.29282	1.65085
C	1.35244	-0.99112	1.16109
C	1.82364	0.31174	0.81911
C	1.69464	1.49669	1.70735
C	0.55833	2.19055	1.70784
C	-0.55522	1.76474	0.81991
C	-1.49928	0.75074	1.16163
H	-2.04132	-1.19650	1.78209
H	-0.13197	-2.36241	1.78204
H	1.96274	-1.86488	0.91024
H	2.75288	0.29631	0.23507
H	2.55192	1.78869	2.32393
H	0.42672	3.08606	2.32517
H	-0.99285	2.58419	0.23531
H	-2.55502	0.89448	0.90931



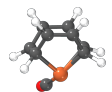
1COT | η^4 center | C_s | Triplet

Fe	0.00000	0.00000	0.00000
C	-1.44311	-0.89151	2.27819
C	-0.34063	-1.66154	2.27860
C	0.79746	-1.42014	1.35852
C	1.54577	-0.21663	1.35840
C	1.39000	0.82685	2.41597
C	0.29723	1.59042	2.41524
C	-0.73546	1.37697	1.35723
C	-1.60777	0.25980	1.35758
H	-2.27780	-1.14114	2.94220
H	-0.28796	-2.53096	2.94287
H	1.25012	-2.31041	0.90749
H	2.52428	-0.26469	0.85745
H	2.15746	0.91730	3.19289
H	0.11768	2.34272	3.19152
H	-1.11798	2.27906	0.85657
H	-2.59952	0.37838	0.90667
C	-0.81648	-1.17120	-1.19161
O	-1.33949	-1.92067	-1.88182



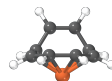
1COT | η^4 edge | C_s | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.57624	0.01691	1.24163
C	-0.48577	-0.73339	1.82780
C	0.83586	-0.27416	1.82782
C	1.22615	0.99064	1.24165
C	0.90067	2.36371	1.68494
C	-0.25138	2.94291	2.07695
C	-1.62757	2.46475	2.07690
C	-2.17227	1.29599	1.68487
H	-2.37477	-0.67007	0.92295
H	-0.63119	-1.80295	2.02486
H	1.61315	-1.02312	2.02487
H	2.27861	0.94681	0.92296
H	1.77157	3.02869	1.68155
H	-0.15823	3.99054	2.38019
H	-2.35027	3.22893	2.38006
H	-3.26786	1.27773	1.68137
C	-0.45556	1.31087	-1.10788
O	-0.78228	2.25338	-1.66997



1COT | η^4 center | C_1 | Singlet

Fe	0.00000	0.00000	0.00000
C	-0.61674	1.62287	2.20921
C	-1.59130	0.69597	2.20508
C	-1.51308	-0.45627	1.27341
C	-0.43542	-1.39889	1.33773
C	0.49245	-1.48947	2.50439
C	1.45341	-0.57136	2.50921
C	1.41469	0.36471	1.34586
C	0.53381	1.49045	1.28243
H	-0.68573	2.50398	2.85480
H	-2.47035	0.80652	2.84780
H	-2.45740	-0.77398	0.81557
H	-0.60809	-2.32738	0.76376
H	0.33166	-2.22143	3.30245
H	2.18722	-0.44620	3.31242
H	2.34977	0.48274	0.76821
H	0.89982	2.41673	0.82502
C	-1.05590	1.15028	-0.93885
O	-1.80465	1.94637	-1.28343

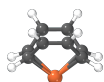


oCOT | η^6 | C_s | Triplet

This is the ground state

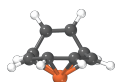
Fe	0.00000	0.00000	0.00000
C	-1.50790	-0.67433	1.16617
C	-0.30036	-1.29045	1.63883
C	1.04416	-0.81545	1.63967
C	1.59650	0.42263	1.16676
C	0.91500	1.64930	0.90711
C	-0.08857	2.24897	1.82689

C	-1.34410	1.80568	1.82655
C	-1.74740	0.70830	0.90622
H	-2.27695	-1.39153	0.85239
H	-0.37250	-2.37510	1.77177
H	1.78137	-1.61417	1.77322
H	2.64536	0.34710	0.85265
H	1.53896	2.38016	0.37677
H	0.23223	3.05569	2.49712
H	-2.10083	2.23213	2.49604
H	-2.69191	0.88531	0.37570



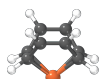
oCOT | η^4 center | C_{2v} | Triplet

Fe	0.00000	0.00000	0.00000
C	-1.39496	-0.92172	2.24042
C	-0.26647	-1.65060	2.24042
C	0.81614	-1.38220	1.25708
C	1.59554	-0.17548	1.25710
C	1.39494	0.92168	2.24048
C	0.26645	1.65056	2.24048
C	-0.81613	1.38220	1.25710
C	-1.59555	0.17548	1.25708
H	-2.20050	-1.15313	2.94697
H	-0.14612	-2.48003	2.94697
H	1.30563	-2.26682	0.82489
H	2.60319	-0.25782	0.82491
H	2.20045	1.15305	2.94707
H	0.14607	2.47996	2.94707
H	-1.30559	2.26682	0.82491
H	-2.60320	0.25785	0.82489



oCOT | η^6 | C_s | Singlet

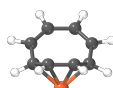
Fe	0.00000	0.00000	0.00000
C	-1.17293	-0.49837	1.58807
C	-0.00509	-1.34410	1.57814
C	1.31085	-1.08289	1.12530
C	1.77240	0.24929	0.85928
C	1.70546	1.39092	1.81495
C	0.63693	2.18332	1.75578
C	-0.47301	1.83901	0.82295
C	-1.43223	0.83706	1.13188
H	-2.08375	-1.10498	1.62793
H	-0.26234	-2.40287	1.68851
H	1.92777	-1.95657	0.88412
H	2.67312	0.27003	0.22353
H	2.53784	1.58110	2.50227
H	0.53416	3.07240	2.38888
H	-0.89636	2.69638	0.28205
H	-2.47873	1.00593	0.85032



oCOT | η^4 center | C_{2v} | Singlet

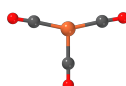
Fe	0.00000	0.00000	0.00000
C	-1.39657	-0.92772	2.25305

C	-0.27127	-1.65454	2.25305
C	0.74238	-1.33925	1.21414
C	1.52605	-0.12590	1.21415
C	1.39656	0.92771	2.25308
C	0.27126	1.65452	2.25308
C	-0.74237	1.33924	1.21415
C	-1.52606	0.12591	1.21414
H	-2.20391	-1.10526	2.97164
H	-0.10107	-2.46345	2.97164
H	1.20692	-2.20138	0.70707
H	2.50293	-0.19475	0.70705
H	2.20389	1.10521	2.97169
H	0.10103	2.46342	2.97169
H	-1.20689	2.20137	0.70705
H	-2.50295	0.19478	0.70707



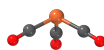
oCOT | η^4 edge | C_s | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.58620	0.02836	1.19884
C	-0.48870	-0.74284	1.75470
C	0.84249	-0.28451	1.75466
C	1.23241	0.99899	1.19887
C	0.90762	2.36613	1.65327
C	-0.24412	2.94608	2.05112
C	-1.62150	2.47192	2.05063
C	-2.17196	1.30586	1.65261
H	-2.39062	-0.65543	0.88304
H	-0.63728	-1.81288	1.94851
H	1.61835	-1.03623	1.94845
H	2.28726	0.95547	0.88295
H	1.77671	3.03467	1.64937
H	-0.14829	3.99180	2.36147
H	-2.34092	3.23714	2.36034
H	-3.26840	1.29785	1.64791



3 | C_{2v} | Triplet
This is the ground state

Fe	0.00000	0.00000	0.00000
C	-1.26515	0.88849	1.04037
C	-1.02614	-0.67214	-1.35960
C	1.70184	-0.60276	-0.46136
O	-2.08320	1.41497	1.63721
O	-1.66816	-1.09324	-2.20992
O	2.71950	-0.99874	-0.79331



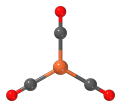
3 | C_{3v} | Triplet

Fe	0.00000	0.00000	0.00000
C	-0.53967	-0.20782	1.75566
C	-1.29864	-0.92226	-0.93788
C	1.46197	-1.12545	-0.11334
O	-0.87451	-0.39995	2.83244
O	-2.09102	-1.54404	-1.48009
O	2.32976	-1.86918	-0.16046



3 | C_s | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.27944	0.22852	1.24245
C	-1.01719	-1.08500	-0.94094
C	1.40560	-1.11563	-0.11018
O	-2.04503	0.21075	2.09581
O	-1.67997	-1.75882	-1.58693
O	2.21782	-1.92283	-0.05120



3 | D_{3h} | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.00186	0.96465	1.20974
C	-0.76975	-0.59975	-1.56383
C	1.77156	-0.36555	0.35454
O	-1.62352	1.56259	1.96122
O	-1.24767	-0.97273	-2.53399
O	2.87079	-0.59320	0.57498



2 | $D_{\infty h}$ | Triplet

This is the ground state

Fe	0.00000	0.00000	0.00000
C	-1.35400	-0.70990	-0.99987
C	1.35455	0.70888	0.99989
O	-2.19991	-1.15375	-1.62476
O	2.20112	1.15145	1.62479



2 | C_{2v} | Triplet

Fe	0.00000	0.00000	0.00000
----	---------	---------	---------

C	-0.95025	-1.29258	-0.93979
C	1.33515	-1.22761	0.40842
O	-1.42197	-2.18560	-1.48160
O	2.07557	-2.08505	0.58205



2 | $D_{\infty h}$ | Singlet

Fe	0.00000	0.00000	0.00000
C	-1.35037	-0.70763	-0.99723
C	1.35065	0.70711	0.99725
O	-2.19565	-1.15085	-1.62132
O	2.19628	1.14964	1.62134



2 | C_{2v} | Singlet

Fe	0.00000	0.00000	0.00000
C	-0.87024	-1.21600	-0.87043
C	1.23312	-1.15571	0.37069
O	-1.43688	-2.03676	-1.44584
O	2.04490	-1.93688	0.60865



1 | $C_{\infty v}$ | Triplet

This is the ground state

Fe	0.00000	0.00000	0.00000
C	1.27070	-1.15142	0.39387
O	2.10102	-1.90379	0.65124



1 | $C_{\infty v}$ | Singlet

Fe	0.00000	0.00000	0.00000
C	1.23166	-1.11606	0.38184
O	2.06265	-1.86905	0.63946

APPENDIX **B**

SUPPLEMENTARY DATA FOR A
REFINED ATOMISTIC MODEL OF
ALKANETHIOL SELF-ASSEMBLED
MONOLAYERS (CHAPTER 4)

B.1 ADDITIONAL ANGLE ANALYSIS RESULTS

BELOW WE PROVIDE THE full set of energy decomposition analysis and tilt angle analysis plots. Figure B.1–Figure B.3 present the energy decomposition analysis for SAMs on Au(100) with the higher density for HDT^{COOH} , HDT^{H} , and HDT^{OH} , in this order. Similarly, Figure B.4–Figure B.6 present the results for Au(100) with the lower density; Figure B.7–Figure B.9 corresponds to Au(111) with higher density, and Figure B.10–Figure B.12, to Au(111) with lower density. Figure B.13–Figure B.24 present the tilt angle scan analyses in that same order.

B.1.1 ENERGY DECOMPOSITION ANALYSIS FOR ALL LIGANDS, SURFACES, AND DENSITIES

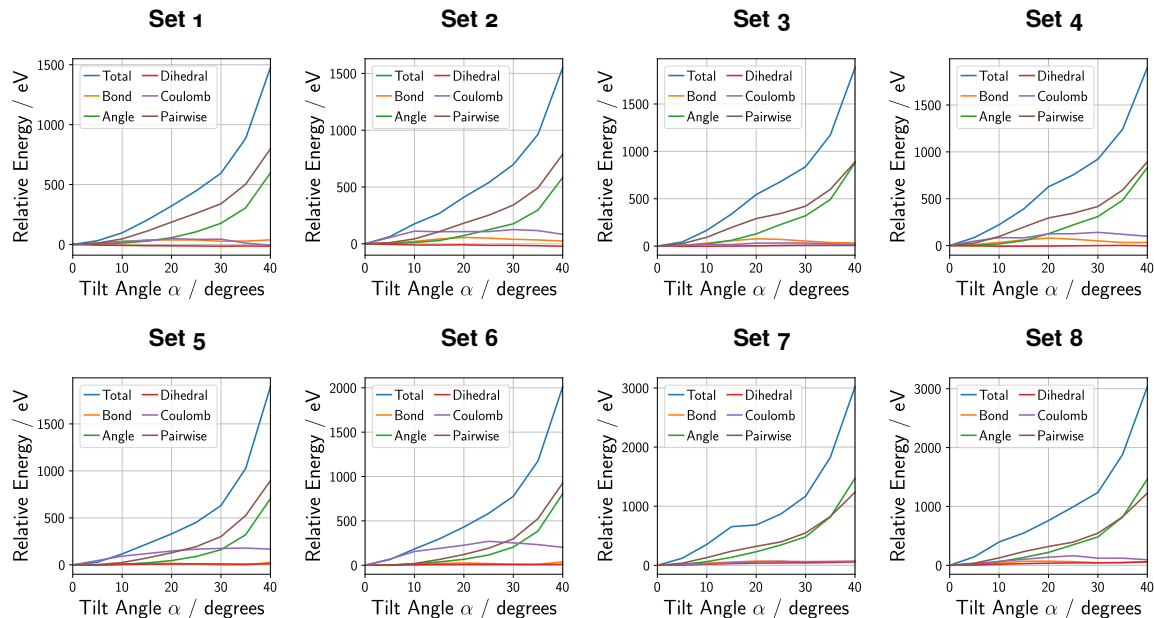


FIGURE B.1 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on Au(100) with a density of 4.73 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

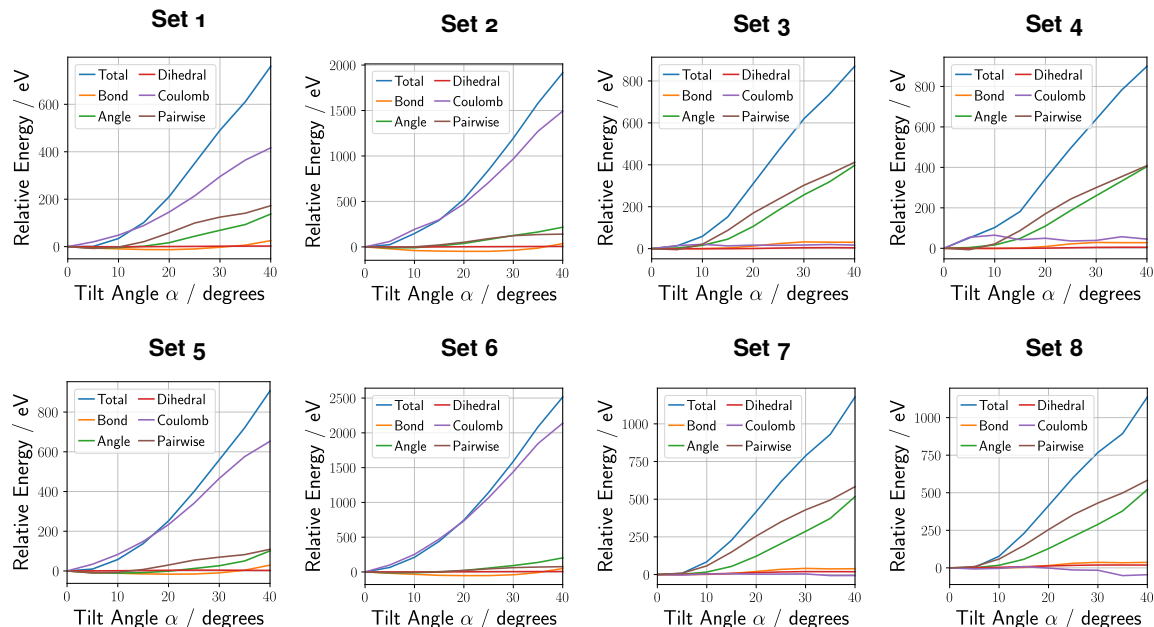


FIGURE B.2 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{H} on Au(100) with a density of 4.73 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

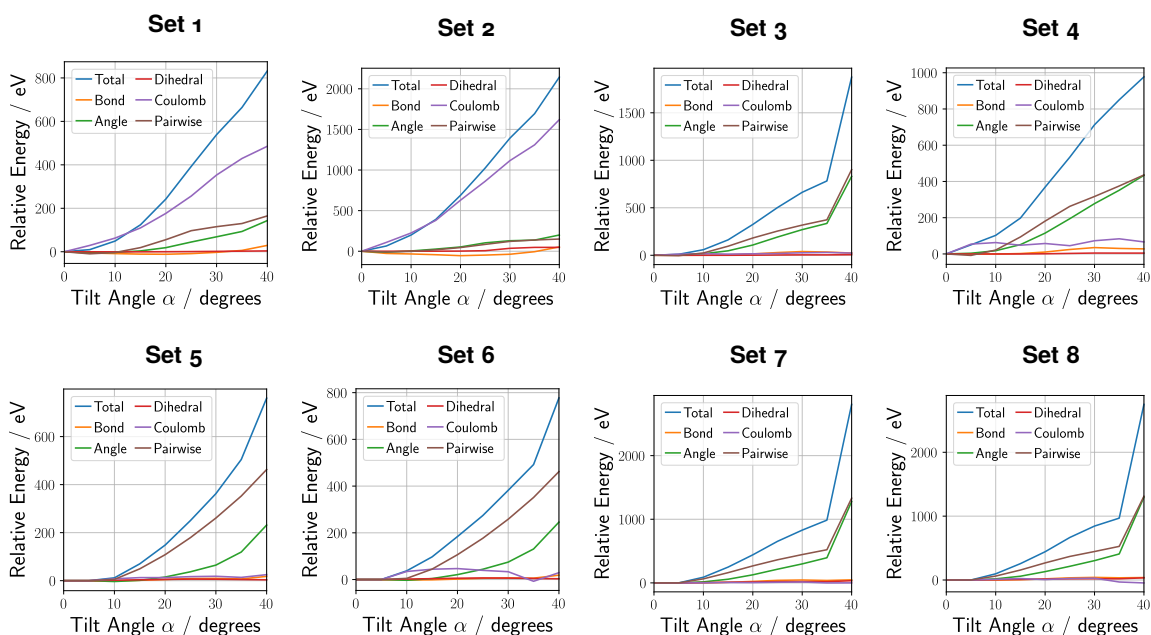


FIGURE B.3 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{OH} on $\text{Au}(100)$ with a density of 4.73 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

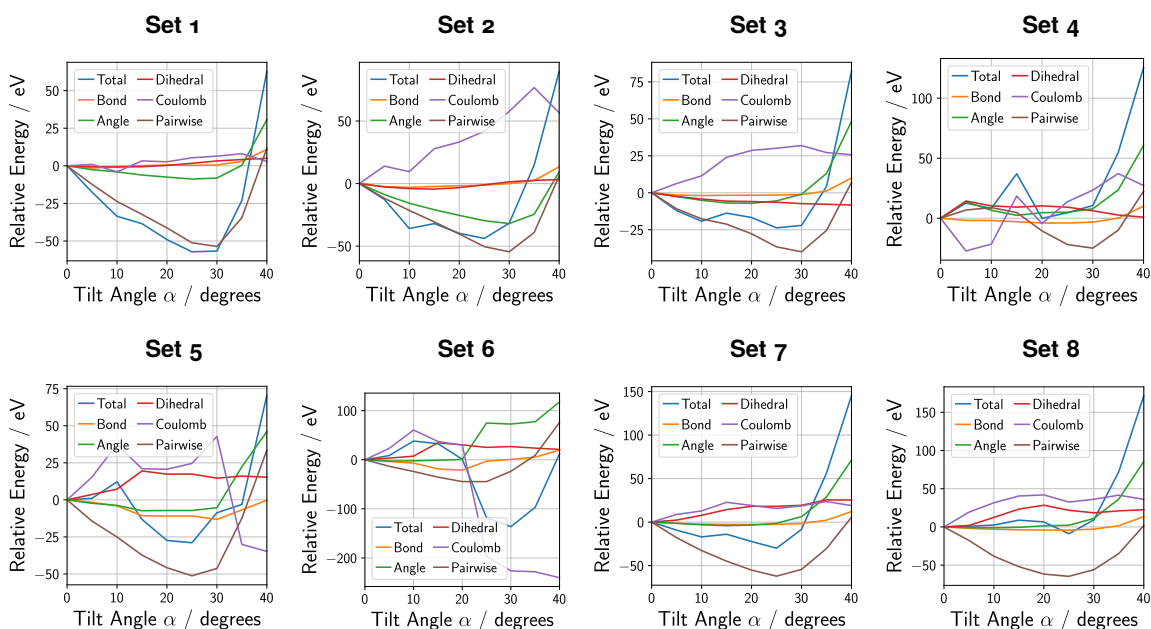


FIGURE B.4 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on $\text{Au}(100)$ with a density of 4.17 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

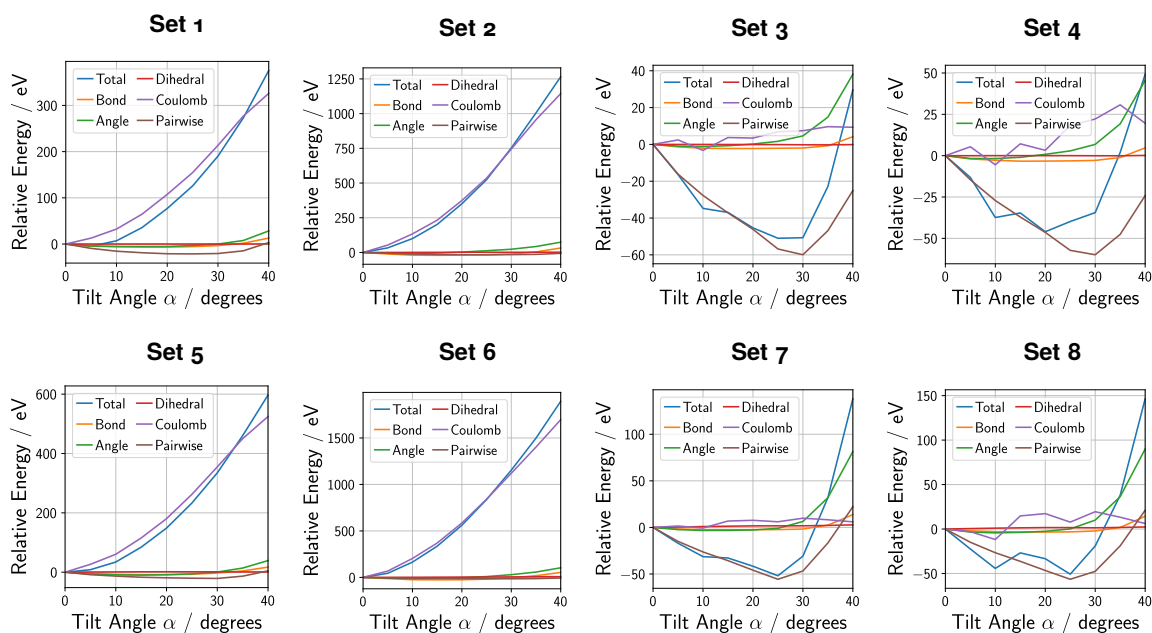


FIGURE B.5 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{H} on $\text{Au}(100)$ with a density of 4.17 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

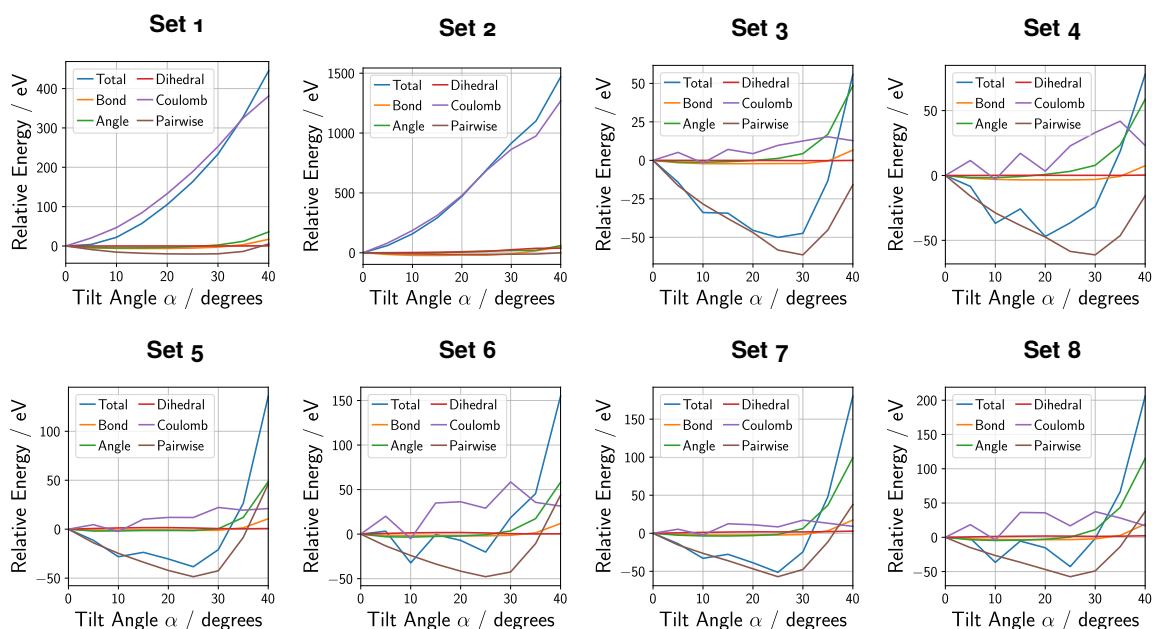


FIGURE B.6 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{OH} on $\text{Au}(100)$ with a density of 4.17 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

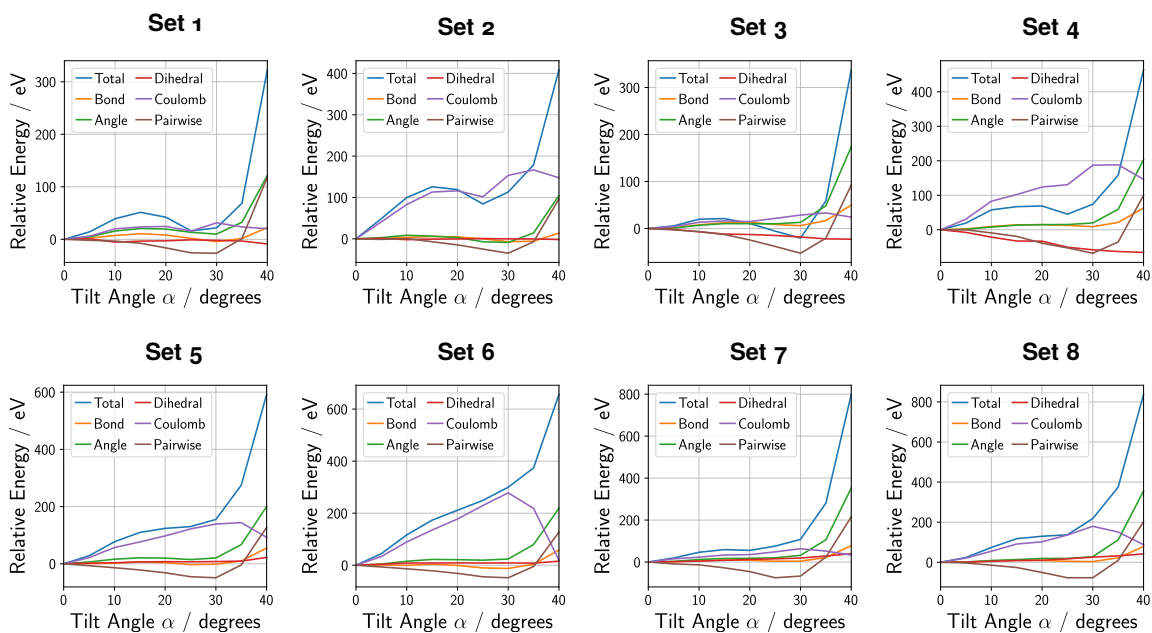


FIGURE B.7 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on Au(111) with a density of 4.67 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

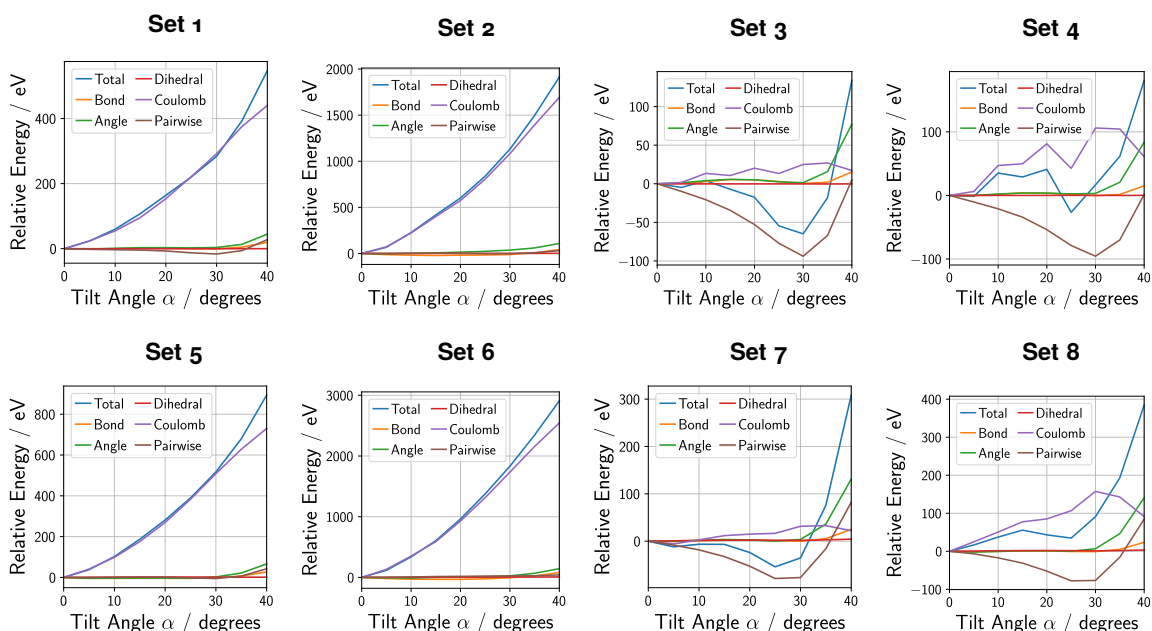


FIGURE B.8 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{H} on Au(111) with a density of 4.67 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

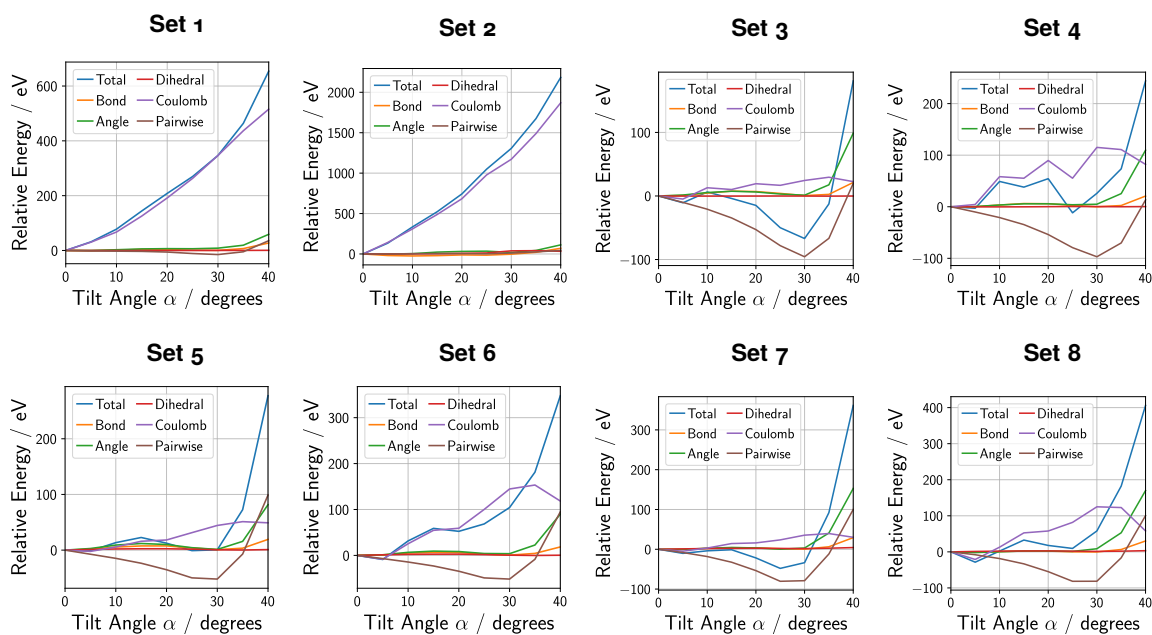


FIGURE B.9 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{OH} on $\text{Au}(111)$ with a density of 4.67 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

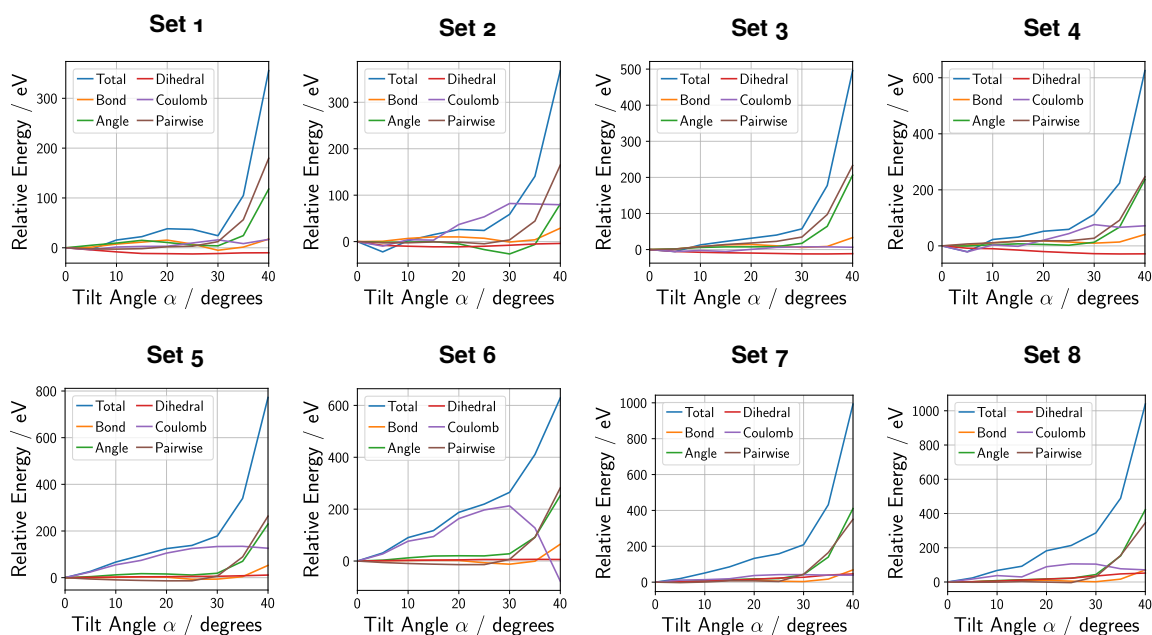


FIGURE B.10 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on $\text{Au}(111)$ with a density of 4.21 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

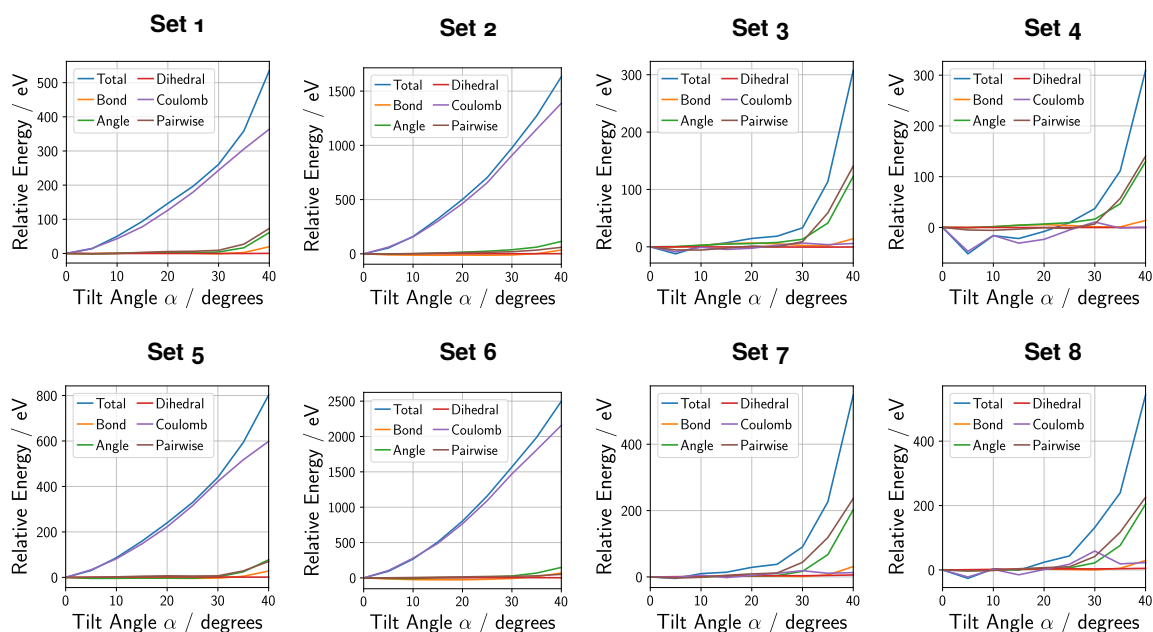


FIGURE B.11 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{H} on $\text{Au}(111)$ with a density of 4.21 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

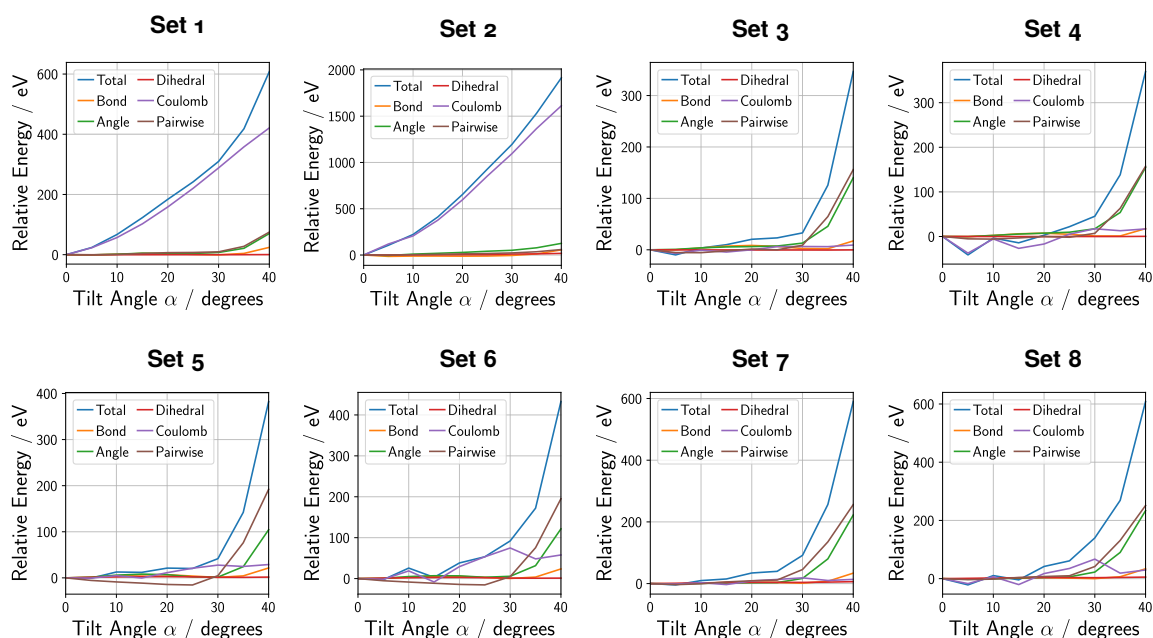


FIGURE B.12 – Energy decomposition analysis as a function of ligand tilt angle for HDT^{OH} on $\text{Au}(111)$ with a density of 4.21 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

B.1.2 TILT ANGLE ANALYSIS FOR ALL LIGANDS, SURFACES, AND DENSITIES

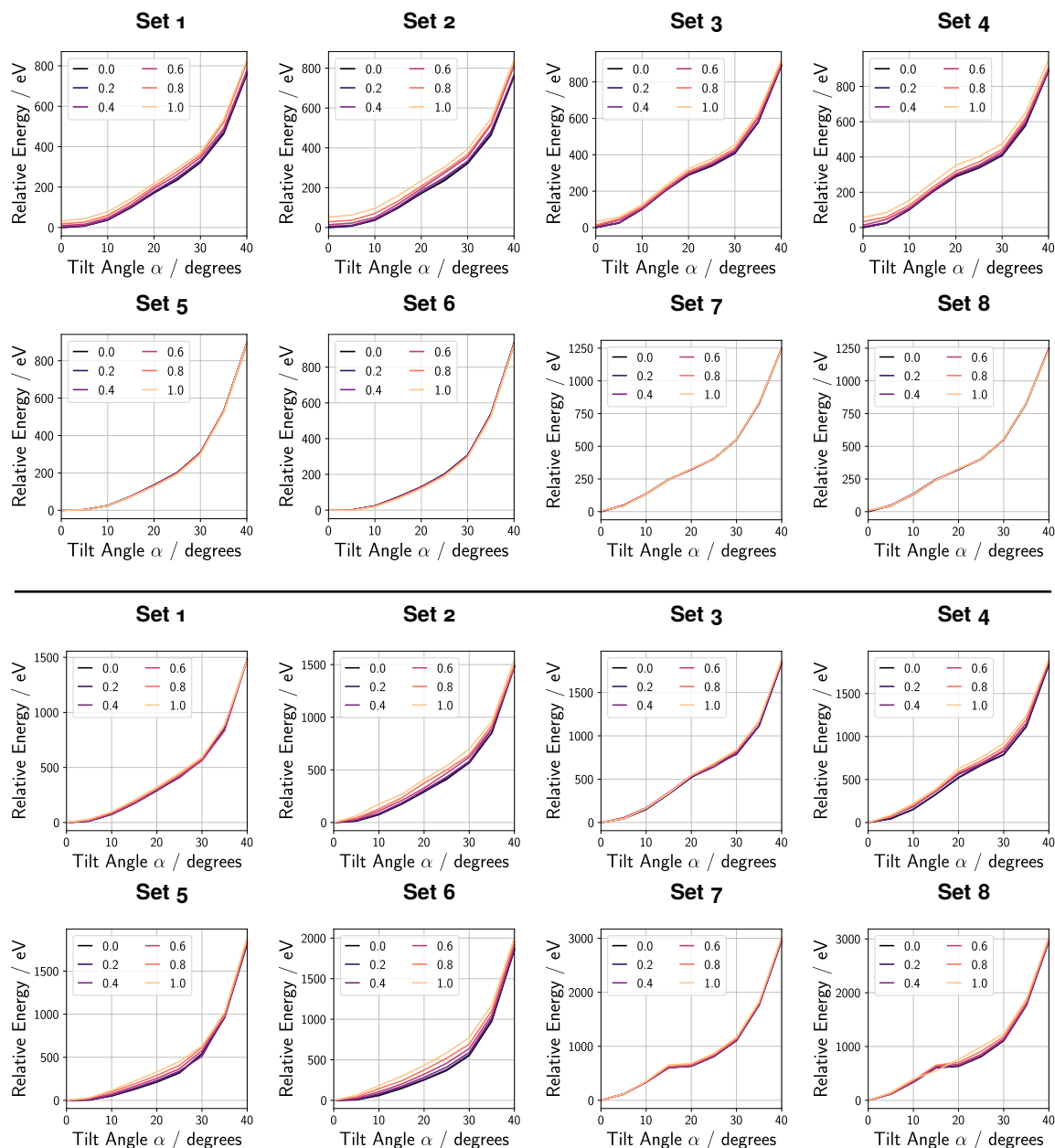


FIGURE B.13 – Ligand tilt angle analysis for HDT^{COOH} on $\text{Au}(100)$ at a density of 4.73 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

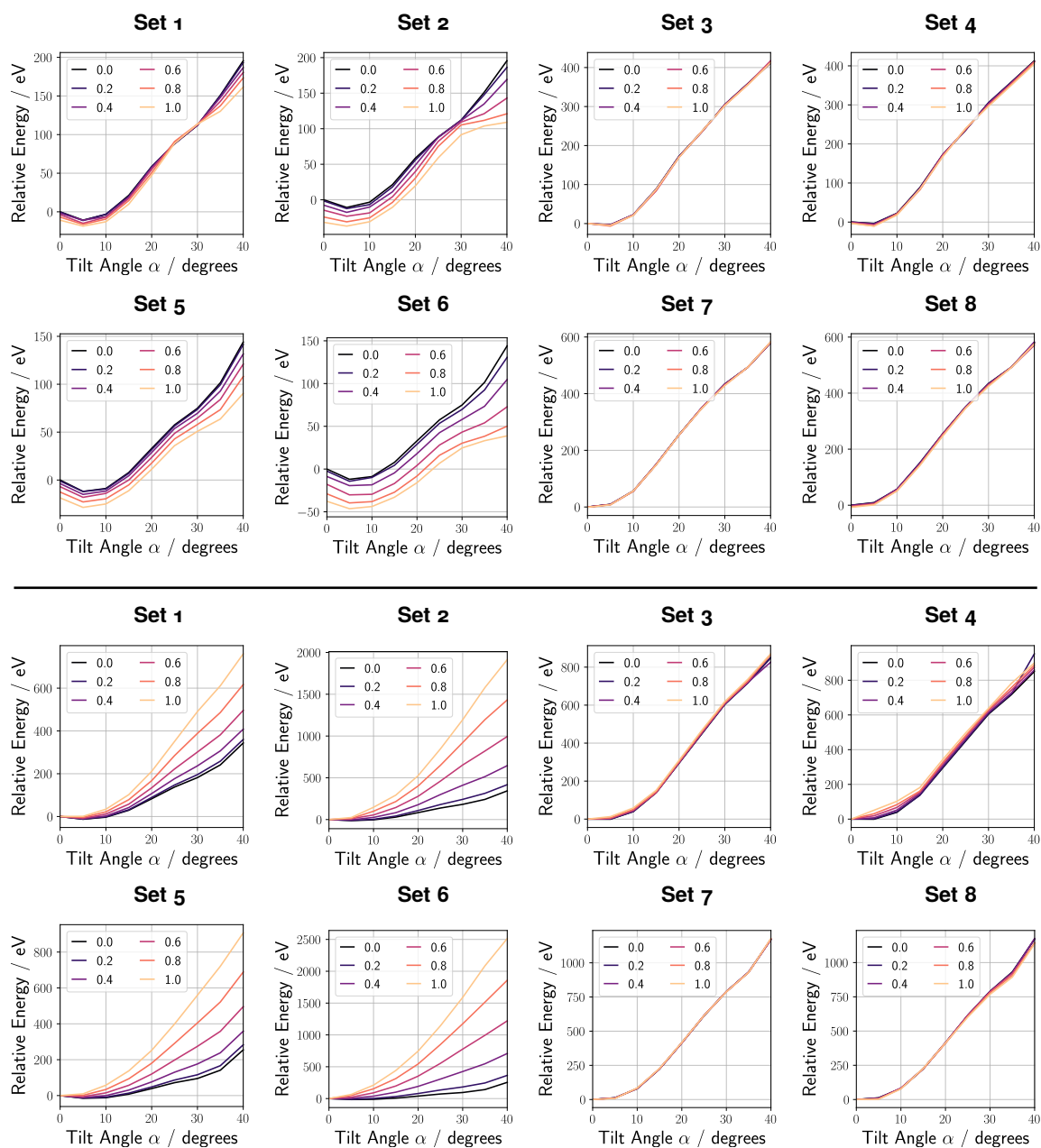


FIGURE B.14 – Ligand tilt angle analysis for HDT^{H} on $\text{Au}(100)$ at a density of 4.73 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

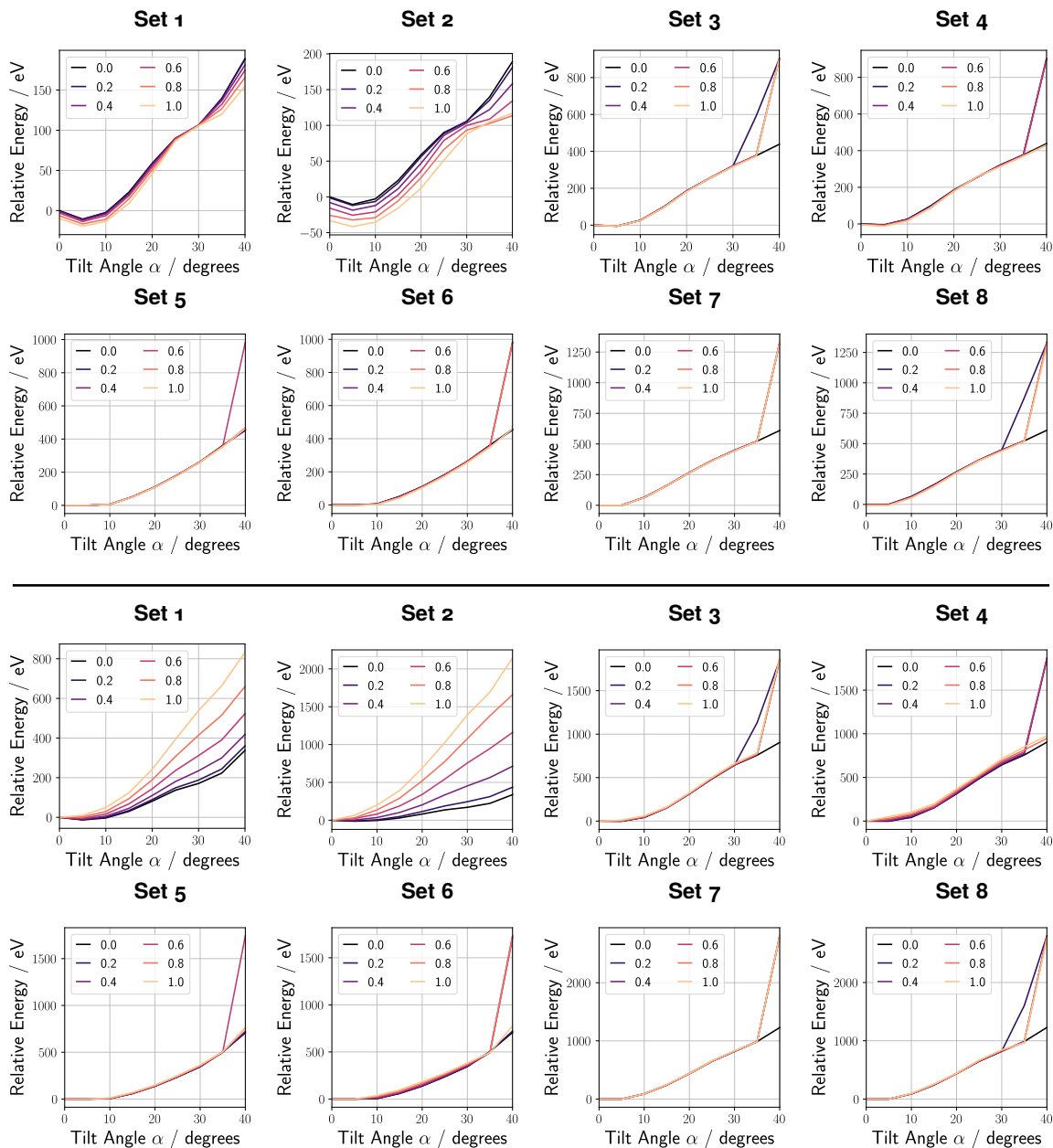


FIGURE B.15 – Ligand tilt angle analysis for HDT^{OH} on $\text{Au}(100)$ at a density of 4.73 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

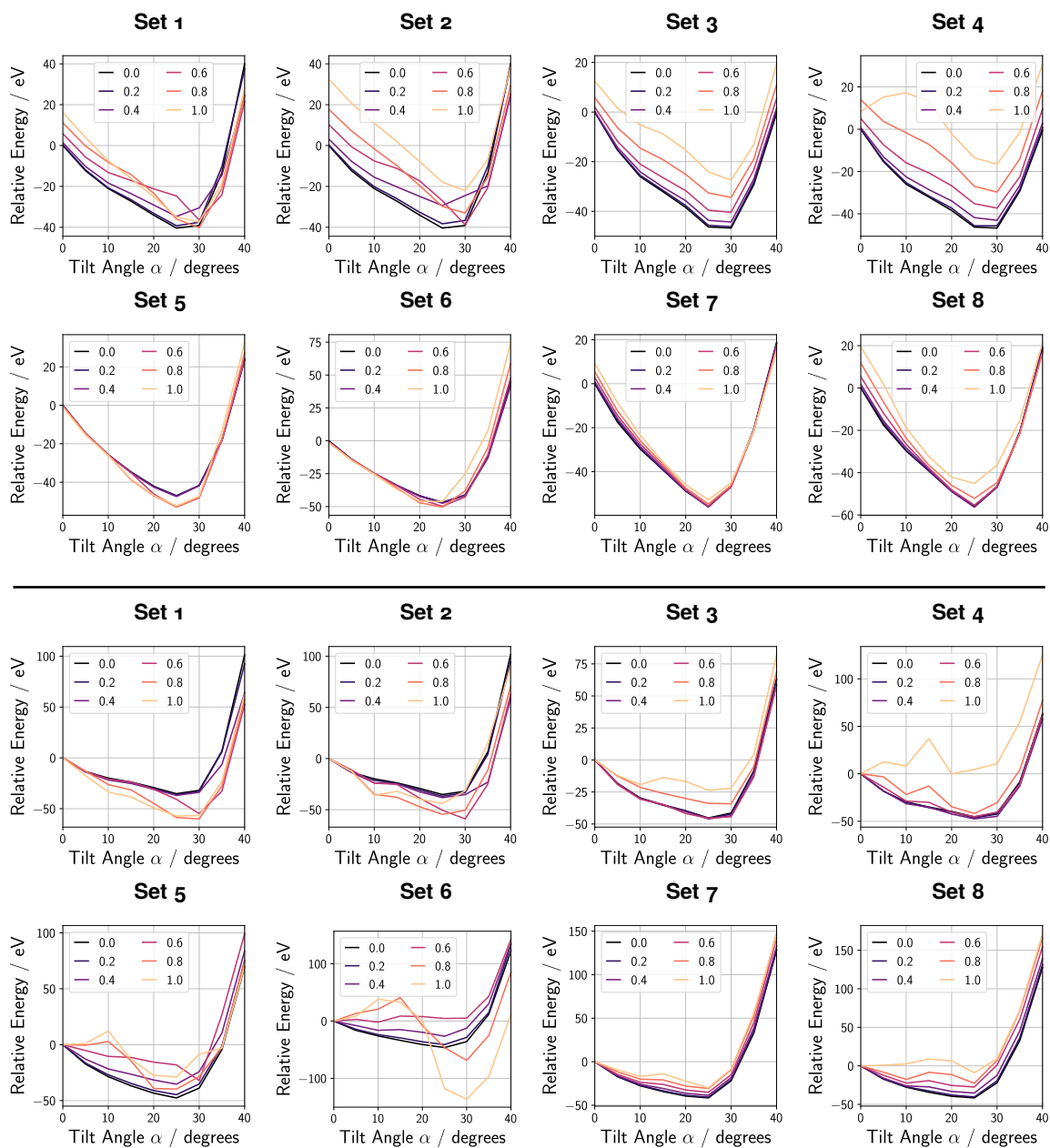


FIGURE B.16 – Ligand tilt angle analysis for HDT^{COOH} on Au(100) at a density of 4.17 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

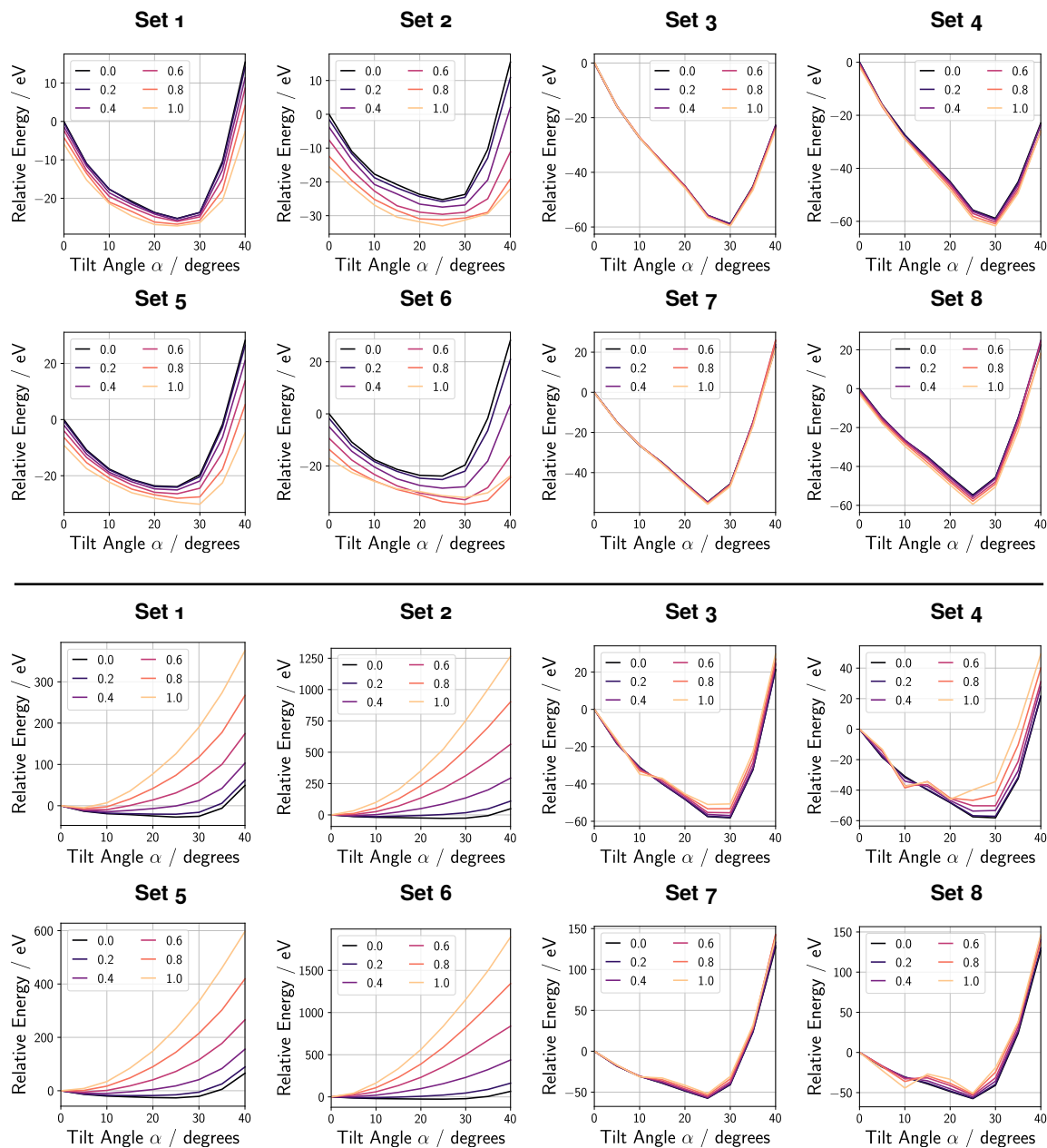


FIGURE B.17 – Ligand tilt angle analysis for HDT^{H} on $\text{Au}(100)$ at a density of 4.17 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

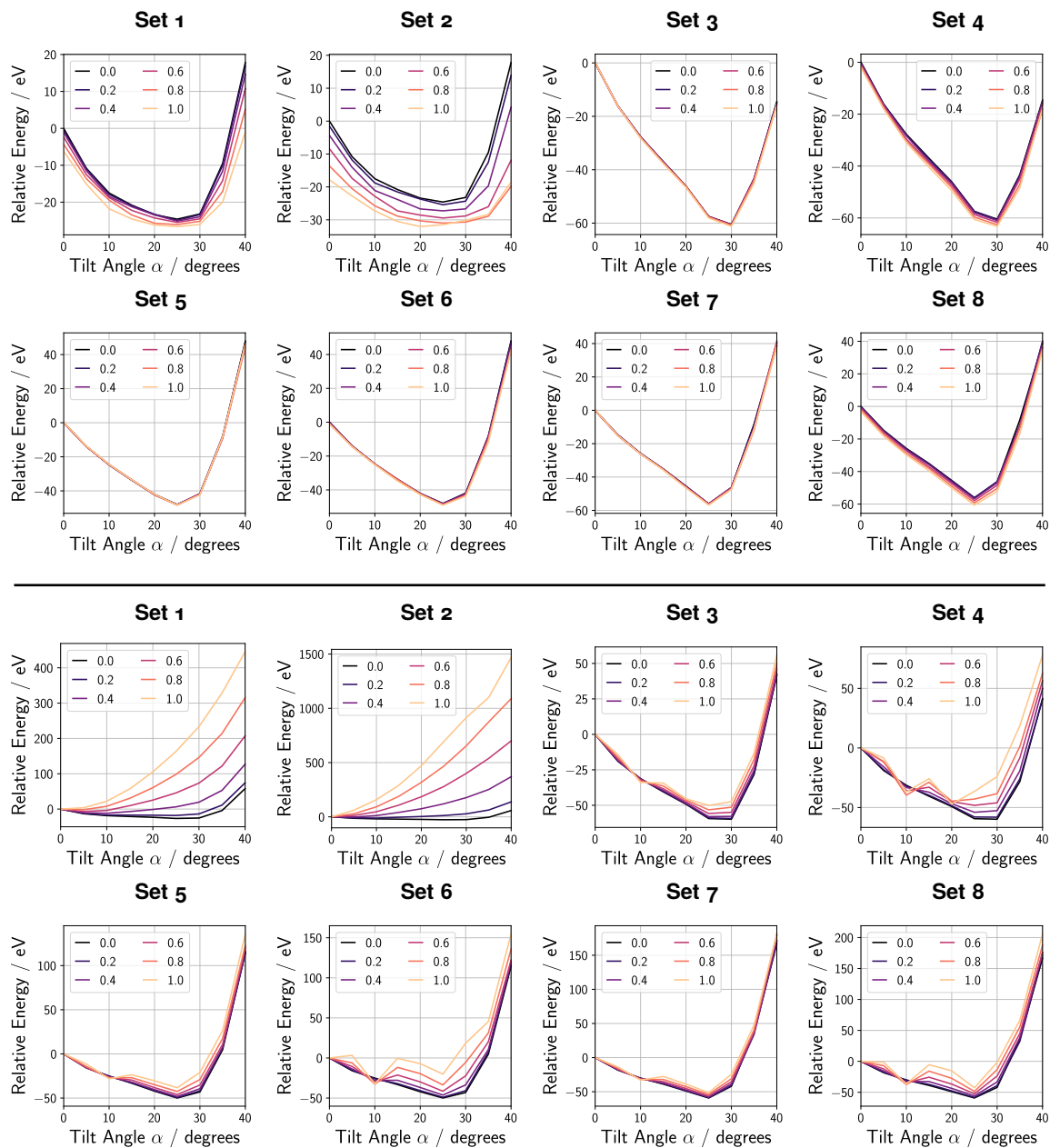


FIGURE B.18 – Ligand tilt angle analysis for HDT^{OH} on $\text{Au}(100)$ at a density of 4.17 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

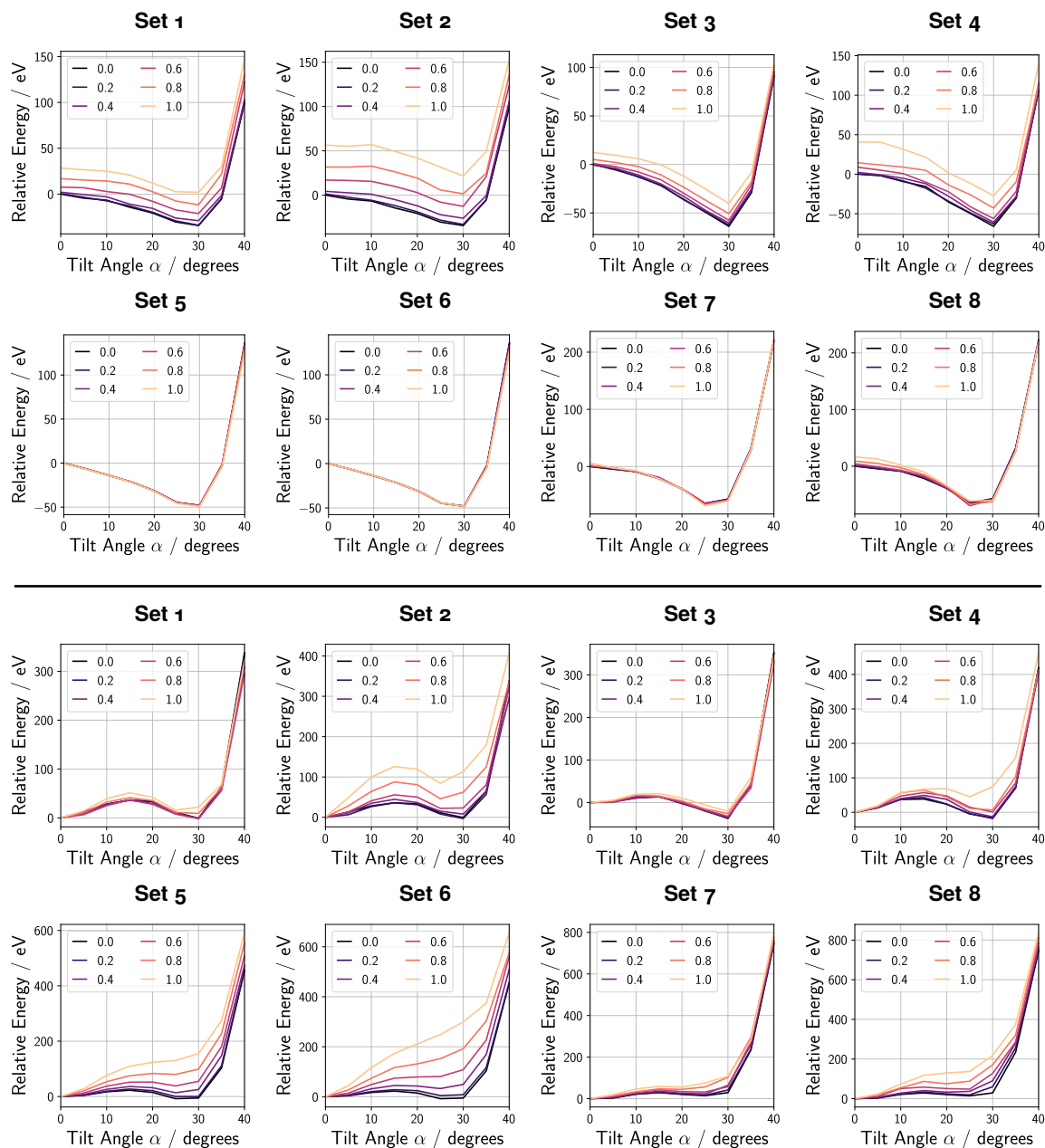


FIGURE B.19 – Ligand tilt angle analysis for HDT^{COOH} on $\text{Au}(111)$ at a density of 4.67 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

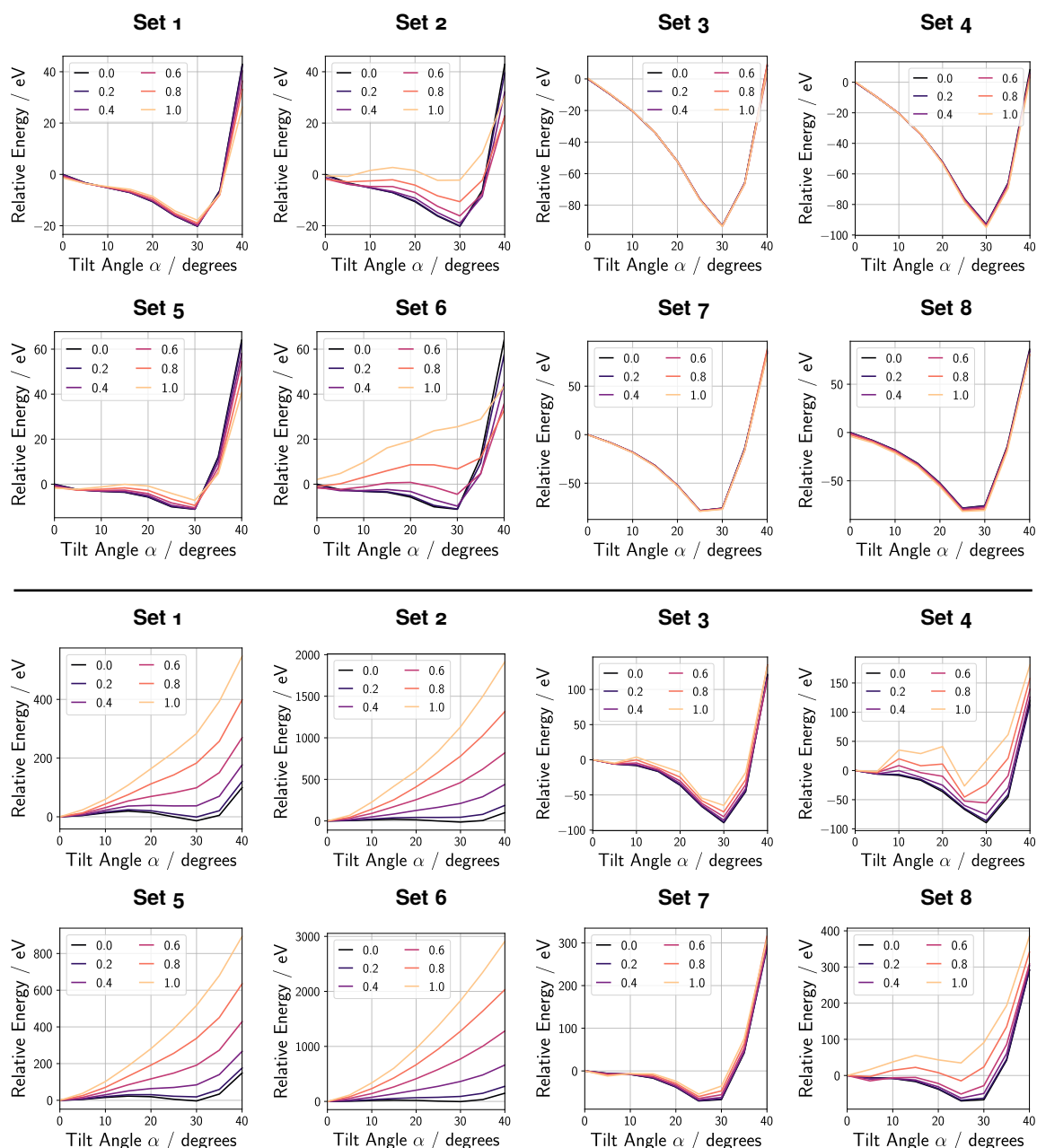


FIGURE B.20 – Ligand tilt angle analysis for HDT^{H} on Au(111) at a density of 4.67 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

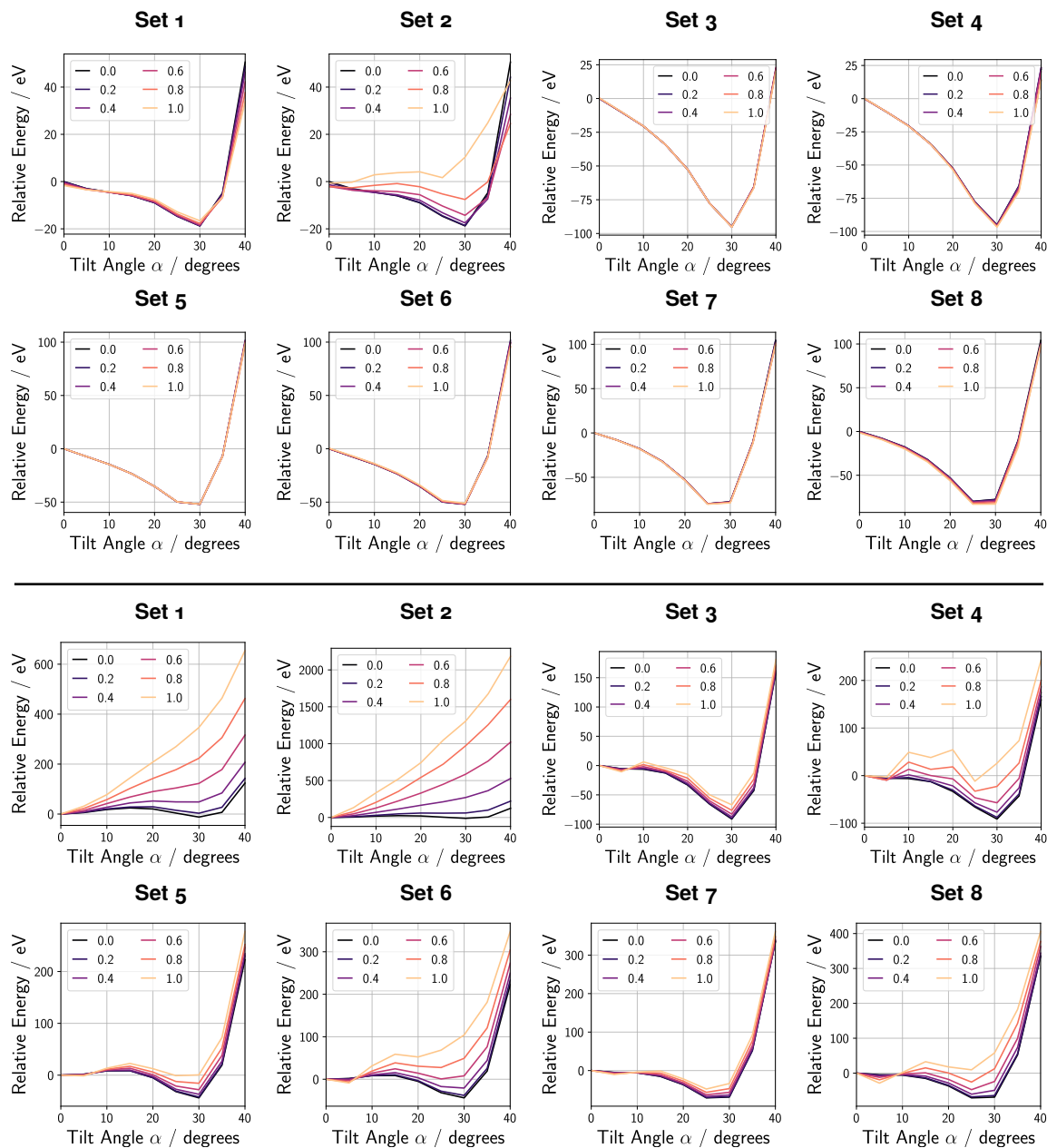


FIGURE B.21 – Ligand tilt angle analysis for HDT^{OH} on $\text{Au}(111)$ at a density of 4.67 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

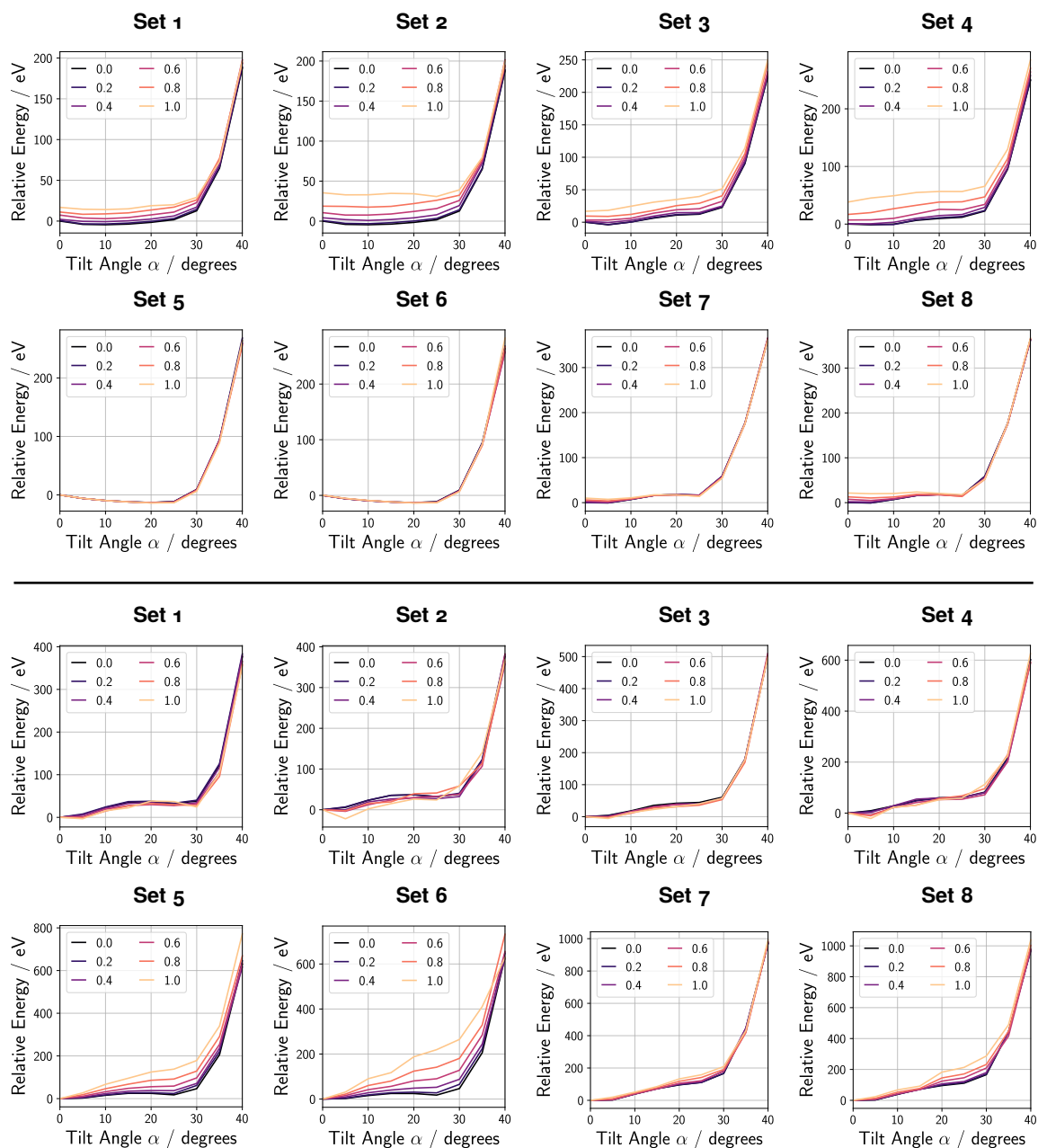


FIGURE B.22 – Ligand tilt angle analysis for HDT^{COOH} on Au(111) at a density of 4.21 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

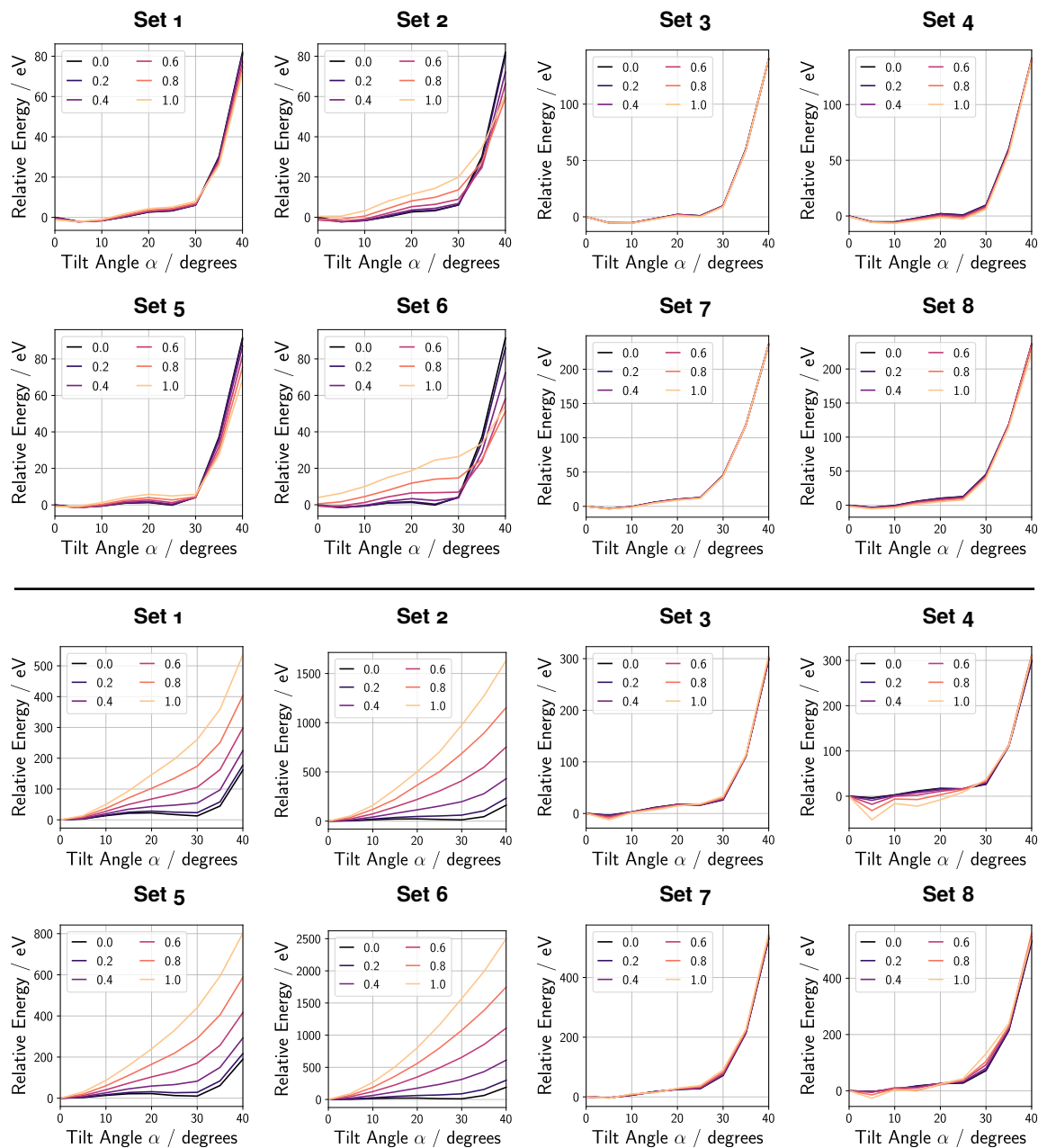


FIGURE B.23 – Ligand tilt angle analysis for HDT^H on Au(111) at a density of 4.21 nm⁻². Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

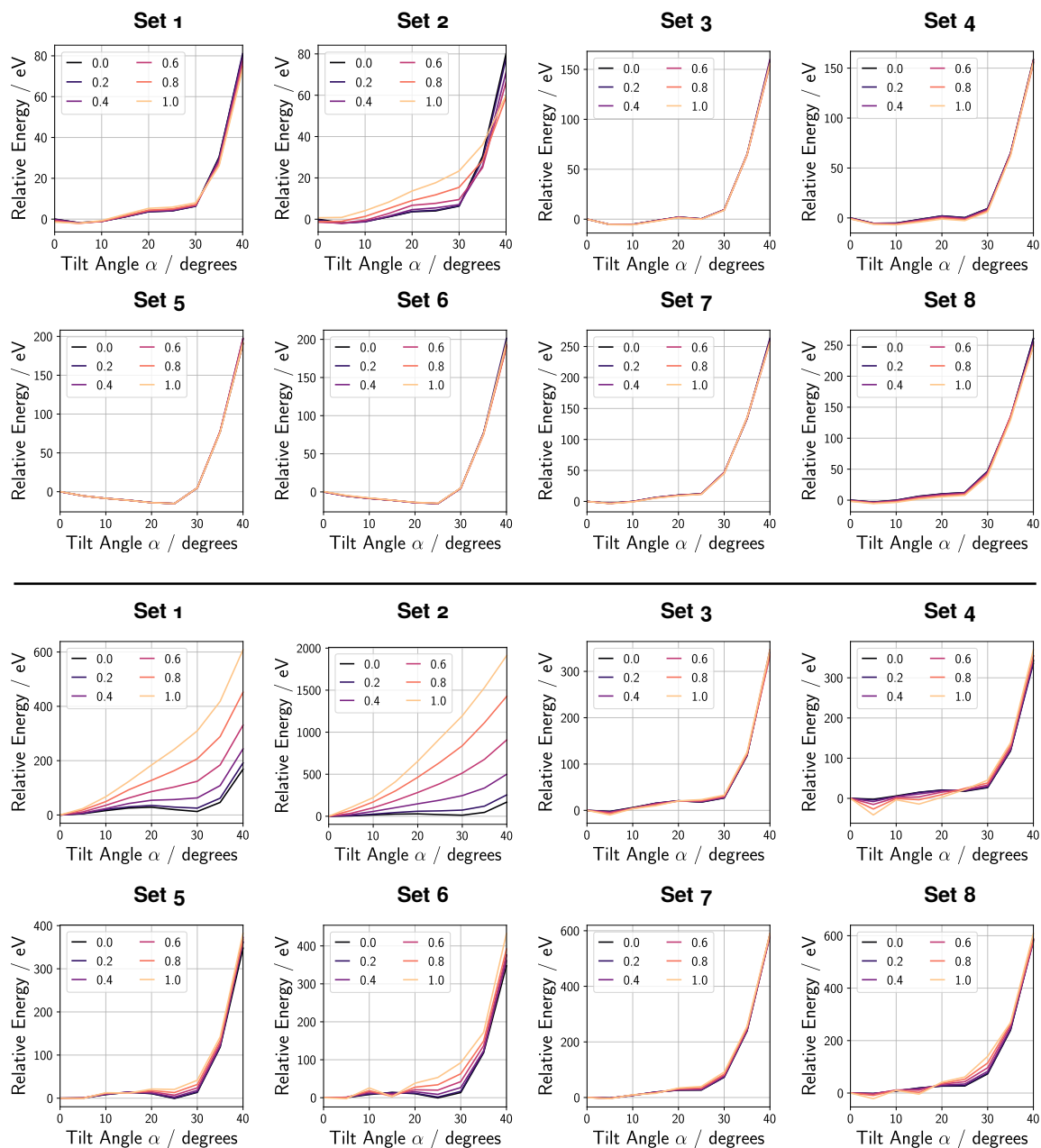


FIGURE B.24 – Ligand tilt angle analysis for HDT^{OH} on $\text{Au}(111)$ at a density of 4.21 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge damping factors.

B.1.3 FINAL GEOMETRIES FOR SAMs ON Au(111)

HERE WE PRESENT THE analysis of the final geometries, as presented in Figure 4.7, for all three ligands on Au(111).

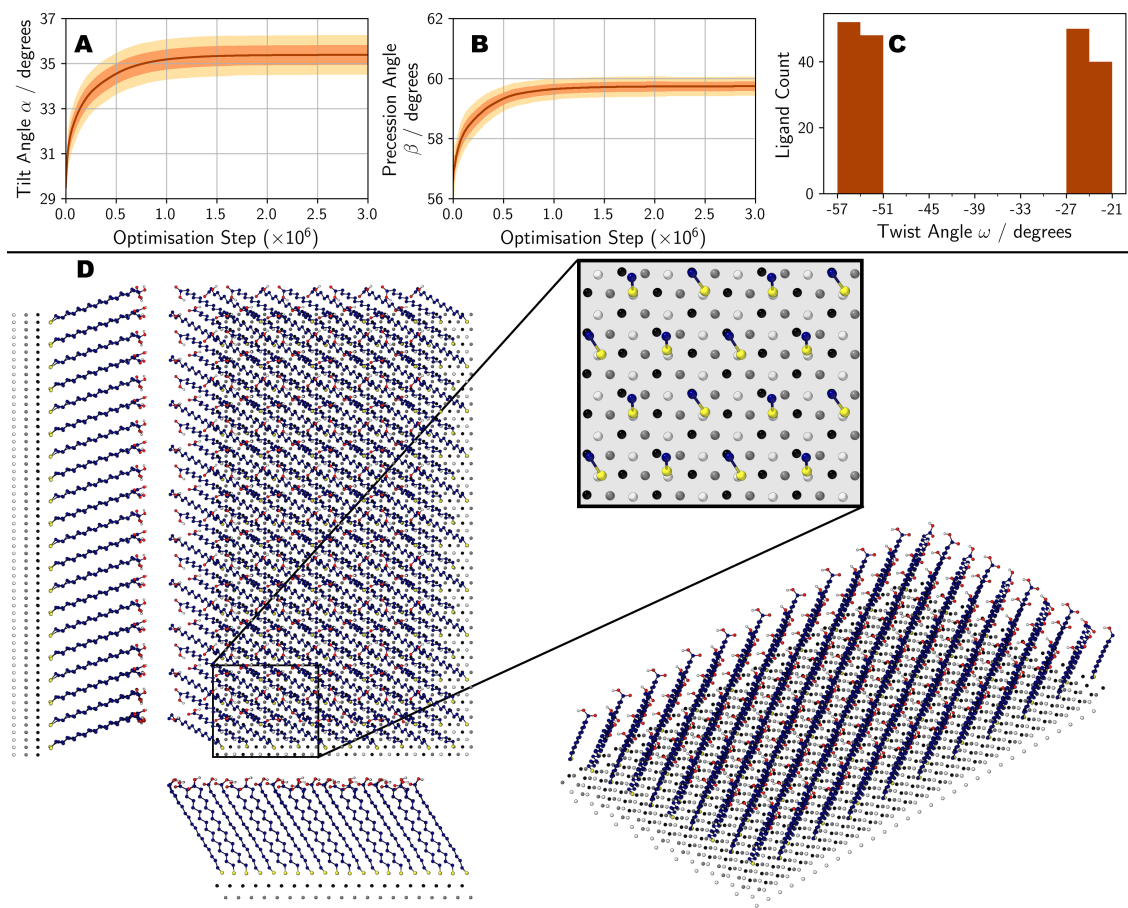


FIGURE B.25 – Final HDT^{COOH} SAM model on Au(111) surface after 3 000 000 optimisation steps. The initial geometry replicates the $(\sqrt{3} \times \sqrt{3})$ R30° adsorption pattern and $c(4 \times 2)$ superlattice packing, consistent with Structure III from Zhang, Goddard & Jiang [342]. Blue spheres: carbon; yellow spheres: sulphur; red spheres: oxygen; white spheres (on chains): hydrogen; black, grey, and white spheres: top, middle, and bottom gold layers, respectively. (A) Evolution of the ligand tilt angle α during the optimisation; (B) evolution of the precession (azimuthal) angle β during the optimisation. In both cases, solid lines show mean values, while shaded areas represent one (orange) and two (yellow) standard deviations. (C) Histogram of the twist angles ω after optimisation. (D) Top and side orthographic projections, along with a perspective view, illustrating the final system's geometry. The inset in (D) provides a closer view of the sulphur atom arrangement, showing only the carbon atoms directly attached to the sulphurs for clarity. Hydrogen atoms from the hydrocarbon portion and the two bottommost gold layers are omitted for clarity. The edges of the system were trimmed for clearer visualisation.

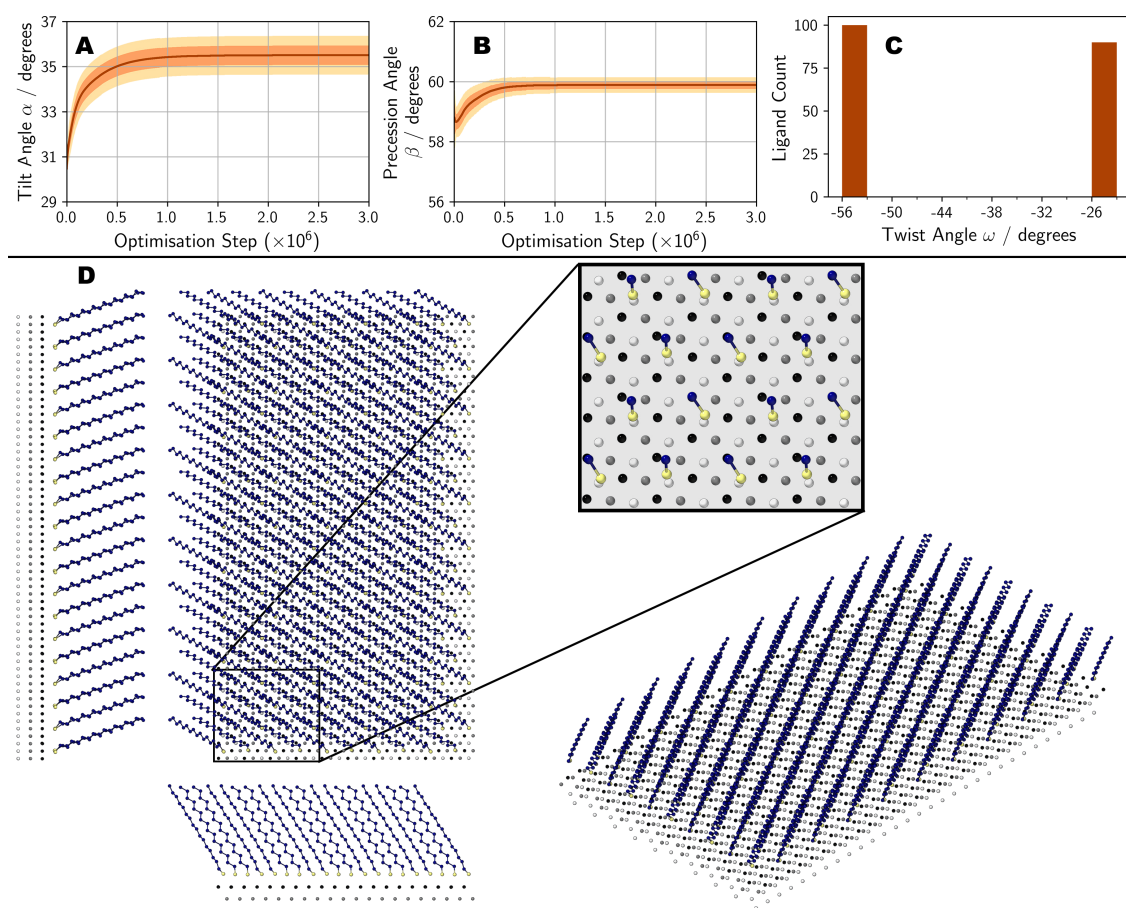


FIGURE B.26 – Final HDT^{H} SAM model on Au(111) surface after 3 000 000 optimisation steps. The initial geometry replicates the $(\sqrt{3} \times \sqrt{3})$ R30° adsorption pattern and $c(4 \times 2)$ superlattice packing, consistent with Structure III from Zhang, Goddard & Jiang [342]. Blue spheres: carbon; yellow spheres: sulphur; black, grey, and white spheres: top, middle, and bottom gold layers, respectively. (A) Evolution of the ligand tilt angle α during the optimisation; (B) evolution of the precession (azimuthal) angle β during the optimisation. In both cases, solid lines show mean values, while shaded areas represent one (orange) and two (yellow) standard deviations. (C) Histogram of the twist angles ω after optimisation. (D) Top and side orthographic projections, along with a perspective view, illustrating the final system's geometry. The inset in (D) provides a closer view of the sulphur atom arrangement, showing only the carbon atoms directly attached to the sulphurs for clarity. Hydrogen atoms and the two bottommost gold layers are omitted for clarity. The edges of the system were trimmed for clearer visualisation.

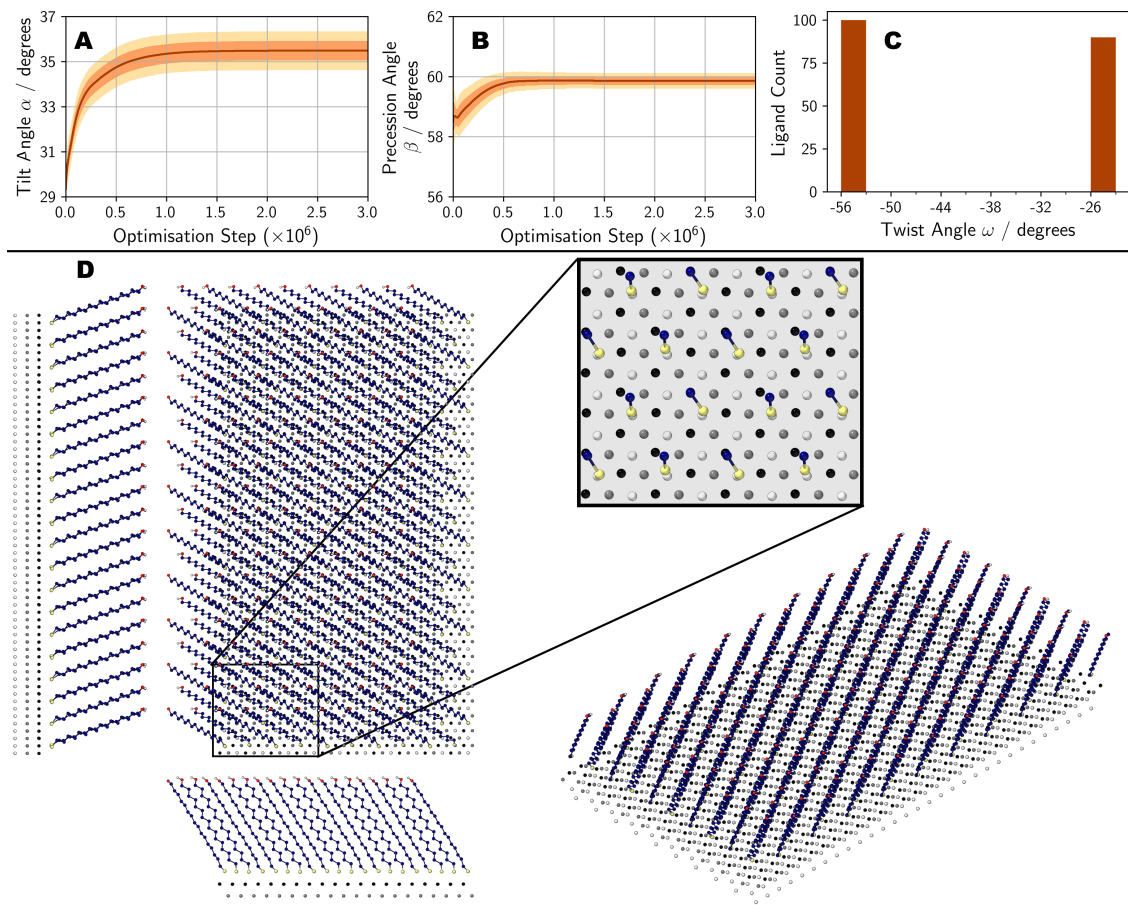


FIGURE B.27 – Final HDT^{OH} SAM model on Au(111) surface after 3 000 000 optimisation steps. The initial geometry replicates the $(\sqrt{3} \times \sqrt{3})$ R30° adsorption pattern and $c(4 \times 2)$ superlattice packing, consistent with Structure III from Zhang, Goddard & Jiang [342]. Blue spheres: carbon; yellow spheres: sulphur; red spheres: oxygen; white spheres (on chains): hydrogen; black, grey, and white spheres: top, middle, and bottom gold layers, respectively. (A) Evolution of the ligand tilt angle α during the optimisation; (B) evolution of the precession (azimuthal) angle β during the optimisation. In both cases, solid lines show mean values, while shaded areas represent one (orange) and two (yellow) standard deviations. (C) Histogram of the twist angles ω after optimisation. (D) Top and side orthographic projections, along with a perspective view, illustrating the final system's geometry. The inset in (D) provides a closer view of the sulphur atom arrangement, showing only the carbon atoms directly attached to the sulphurs for clarity. Hydrogen atoms from the hydrocarbon portion and the two bottommost gold layers are omitted for clarity. The edges of the system were trimmed for clearer visualisation.

B.2 GEOMETRIES, TOPOLOGIES, AND FORCE FIELD PARAMETERS

THIS SECTION PROVIDES A comparison between key parameters discussed in the main text as well as links for all relevant files utilised in the simulations in readily usable format. The functional forms of the Morse and LJ potentials defined for the files are discussed in § 2.2.1

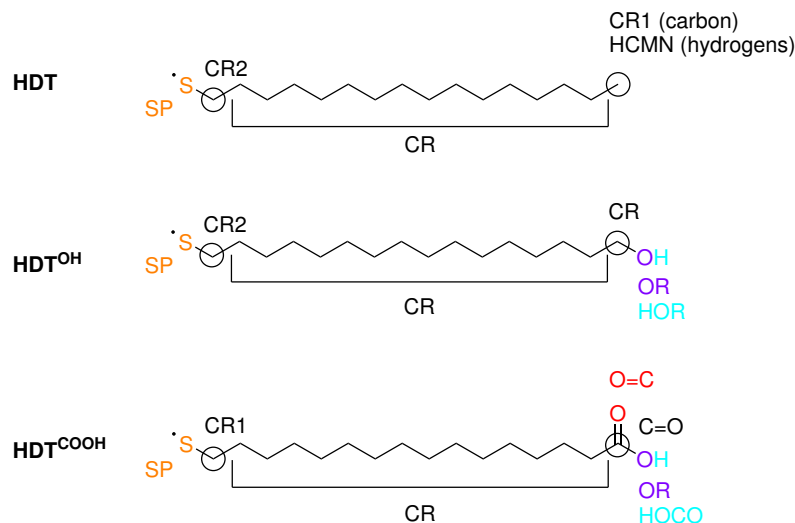


FIGURE B.28 – Atom types for the different ligands as defined in the cGenFF. Hydrogens not designated in the figure are labelled HCMM.

TABLE B.1 – cGenFF and NBO partial charges (in Coulomb) for all ligand atoms.

Atom Type	CGenFF	NBO*	Description
CR	-0.18	-0.37	Non-terminal carbon atoms
CR ₁ [†] (HDT ^H)	-0.27	-0.58	Terminal group carbon atom
CR ₁ [†] (HDT ^{OH})	0.05	-0.05	Terminal group carbon atom (connected to -OH)
CR ₂ [†]	-0.38	-0.56	Carbon atom connected to head-group (S)
C=O	0.80	0.77	Carbonyl carbon atom
HCMH	0.09	0.19	Hydrogen atoms connected to carbon
HCMN			
HOR	0.42	0.45	-OH hydrogen atom in HDT ^{OH}
HOCO	0.42	0.49	-OH hydrogen atom in HDT ^{COOH}
OR	-0.65	-0.70	-OH oxygen atom in HDT ^{OH} and HDT ^{COOH}
O=C	-0.55	-0.58	Carboxyl oxygen atom in HDT ^{COOH}
SP	0.20	0.10	Sulphur head-group

* The values shown here are representative values for each atom type to facilitate comparison. They differ slightly between ligands and specific atom instances in the chains. See files below for detailed figures.

† These atom types are defined in the cGenFF sets of parameters, but are assigned as CR in the SwissParam sets. We used them here to facilitate differentiation. For HDT^{COOH}, CR₂ in this table reads as CR₁ in the files. For HDT^{OH}, CR₁ in this table reads as CR.

TABLE B.2 – Relevant files utilised in the various MD simulations described in this work. Partial charges are contained in the PSF files. The Finnis–Sinclair potential for Au and the Morse potential for the Au–S interaction is stored in the .pot files, native to MBN EXPLORER. All PSF files are for single molecules. They can be replicated for as many molecules as the system will have.

DFT Optimised Geometries	
HDT ^{COOH} xyz file	HDT-COOH_DFT_Opt.xyz
HDT ^H xyz file	HDT_DFT_Opt.xyz
HDT ^{OH} xyz file	HDT-OH_DFT_Opt.xyz
Sets 1–8 parameter, geometry, and topology files	
HDT^{COOH}	
PDB geometry file Sets 1–4	HDT-COOH_CGenFF.pdb
PDB geometry file Sets 5–8	HDT-COOH_MMFF.pdb
PSF topology file Sets 1,3	HDT-COOH_CGenFF_CGenFF.psf
PSF topology file Sets 2,4	HDT-COOH_CGenFF_NBO.psf
PSF topology file Sets 5,7	HDT-COOH_MMFF_CGenFF.psf
PSF topology file Sets 6,8	HDT-COOH_MMFF_NBO.psf
PRM parameter file Sets 1,2	HDT-COOH_CGenFF.prm
PRM parameter file Sets 3,4	HDT-COOH_CGenFF_UFF.prm
PRM parameter file Sets 7,8	HDT-COOH_MMFF_UFF.prm
PRM parameter file Sets 5,6	HDT-COOH_MMFF.prm
HDT^H	
PDB geometry file Sets 1–4	HDT_CGenFF.pdb
PDB geometry file Sets 5–8	HDT_MMFF.pdb
PSF topology file Sets 1,3	HDT_CGenFF_CGenFF.psf
PSF topology file Sets 2,4	HDT_CGenFF_NBO.psf
PSF topology file Sets 5,7	HDT_MMFF_CGenFF.psf
PSF topology file Sets 6,8	HDT_MMFF_NBO.psf
PRM parameter file Sets 1,2	HDT_CGenFF.prm
PRM parameter file Sets 3,4	HDT_CGenFF_UFF.prm
PRM parameter file Sets 5,6	HDT_MMFF.prm
PRM parameter file Sets 7,8	HDT_MMFF_UFF.prm
HDT^{OH}	
PDB geometry file Sets 1–4	HDT-OH_CGenFF.pdb
PDB geometry file Sets 5–8	HDT-OH_MMFF.pdb
PSF topology file Sets 1,3	HDT-OH_CGenFF_CGenFF.psf
PSF topology file Sets 2,4	HDT-OH_CGenFF_NBO.psf
PSF topology file Sets 5,7	HDT-OH_MMFF_CGenFF.psf
PSF topology file Sets 6,8	HDT-OH_MMFF_NBO.psf
PRM parameter file Sets 1,2	HDT-OH_CGenFF.prm
PRM parameter file Sets 3,4	HDT-OH_CGenFF_UFF.prm
PRM parameter file Sets 5,6	HDT-OH_MMFF.prm
PRM parameter file Sets 7,8	HDT-OH_MMFF_UFF.prm
General POT file containing Au Finnis-Sinclair and Au–S Morse parameters	Potential.pot
Final Unit Cell Geometries, Topologies, and FF Parameters	
HDT^{COOH}	
PDB geometry file	HDT-COOH_Final_Unit_Cell.pdb
PSF topology file	HDT-COOH_Final.psf
PRM parameter file	HDT-COOH_Final.prm
HDT^H	
PDB geometry file	HDT_Final_Unit_Cell.pdb

PSF topology file
PRM parameter file

HDT_Final.psf
HDT_Final.prm

HDT^{OH}

PDB geometry file
PSF topology file
PRM parameter file

HDT-OH_Final_Unit_Cell.pdb
HDT-OH_Final.psf
HDT-OH_Final.prm

General POT file containing Au Finnis–Sinclair and Au–S Morse parameters Potential_Final.pot

APPENDIX

C

PUBLICATIONS AND CONFERENCE PRESENTATIONS

C.1 FIRST-AUTHOR PUBLICATIONS

- 1 **C P Souza** and F Fantuzzi, “Computational strategies for modelling excited states in organometallic chemistry”, in *Organometallic Chemistry*, ed C Bakewell, G R Owen, N Costa and R Musgrave, Royal Society of Chemistry, London, 2024, vol 45, chap 9, pp 271–316, DOI: 10.1039/9781837676200-00271

Computational strategies for modelling excited states in organometallic chemistry[†]

Cauê P. Souza and Felipe Fantuzzi*

DOI: 10.1039/9781837676200-00271

This chapter explores advanced computational methods and strategies to model excited states in organometallic systems, essential for advancing discovery, design, and comprehension in fields such as photocatalysis, artificial photosynthesis, and light-responsive materials. We initiate with a fundamental discussion on available quantum mechanical approaches for organometallic compounds, stressing the importance of carefully choosing theoretical methods that are specifically suited to their unique characteristics. We delineate the theoretical underpinnings and practical applications of various electronic structure methods, including density functional theory (DFT) and post-Hartree–Fock approaches, and detail their adaptability to the unique properties of transition metal complexes. Particular attention is given to multireference and perturbative methods, which are critical for accurately describing the complex electronic structure typical of organometallic compounds. Through hierarchical classification, critical evaluation, and carefully curated references, this chapter

- 2 **C P Souza**, A V Verkhovtsev, N J Mason, A V Solov'yov and F Fantuzzi, “A refined atomistic model of functionalized self-assembled monolayers on gold: Assessment of force field parameters”, *J Chem Phys*, 2025, **163**, 094704, DOI: 10.1063/5.0274290

The Journal
of Chemical Physics

ARTICLE

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A refined atomistic model of functionalized self-assembled monolayers on gold: Assessment of force field parameters

Cite as: *J. Chem. Phys.* **163**, 094704 (2025); doi: 10.1063/5.0274290
Submitted: 4 April 2025 • Accepted: 29 June 2025 •
Published Online: 3 September 2025



Cauê P. Souza,^{1,a)} Alexey V. Verkhovtsev,² Nigel J. Mason,³ Andrey V. Solov'yov,² and Felipe Fantuzzi^{1,b)}

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³ Physics and Astronomy, School of Engineering, Mathematics and Physics, University of Kent, Park Wood Rd, Canterbury CT2 7NH, United Kingdom

This work featured in SciLight:

B Ikenson, “Advancing the understanding of self-assembled monolayers”, *Scilight*, 2025, **2025**, 361105, DOI: 10.1063/10.0039292

- 3 **C P Souza**, A V Verkhovtsev, A V Walker, N J Mason, A V Solov'yov, L McElwee-White, M Zlatar and F Fantuzzi, "Excited-state dissociation of (η^4 -diene)Ru(CO)₃ precursors for photo-assisted chemical vapour deposition", *Phys Chem Chem Phys*, 2026, **28**, 17804–17817, DOI: 10.1039/d6cp00843g

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Cite this: *Phys. Chem. Chem. Phys.*, 2026, 28, 17804

Excited-state dissociation of (η^4 -diene)Ru(CO)₃ precursors for photo-assisted chemical vapour deposition

Cauê P. Souza,^a Alexey V. Verkhovtsev,^b Amy V. Walker,^c Nigel J. Mason,^d Andrey V. Solov'yov,^b Lisa McElwee-White,^e Matija Zlatar^{*,f} and Felipe Fantuzzi^{*,a}

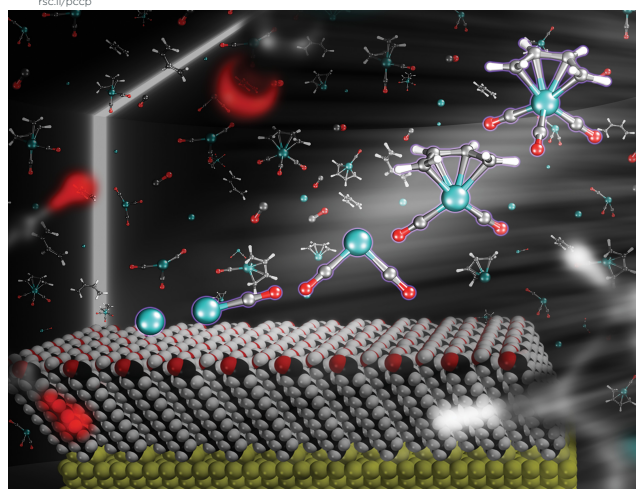
Ruthenium π -diene carbonyl complexes have emerged as promising precursors for photo-assisted chemical vapour deposition (PACVD), yet their photodissociation mechanisms remain unclear. Here we use static quantum-chemical calculations to map the excited-state dissociation landscape of (η^4 -diene)Ru(CO)₃ precursors (diene = BuD, MBuD, CHD, COT, CBuD). Ground-state DFT optimisations and Ru–ligand scans are combined with TD-DFT excitations and adiabatic singlet potential energy surface profiles to identify CO- and diene-loss pathways, while EDA–NOCV and natural transition orbital analyses rationalise the Ru–diene bonding and the character of the bright states that drive reactivity. Calculated UV-vis spectra reproduce experimental trends, including the markedly higher absorptivity and extended wavelength coverage of the COT-containing complex. CO loss is generally enabled by a range of ligand-field or charge-transfer excitations and internal conversion-assisted channels. In contrast, diene loss is strongly ligand dependent: BuD, MBuD, and CHD show accessible pathways, CBuD remains resistant, and COT exhibits additional complexity due to ligand flexibility and coordination changes, all consistent with experiment. These results outline favourable stepwise routes towards unsaturated fragments and provide a basis for future non-adiabatic dynamics, irradiation-driven molecular dynamics

Received 7th March 2026,
Accepted 18th May 2026
DOI: 10.1039/d6cp00843g

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Matija Zlatar, Felipe Fantuzzi et al.
Excited-state dissociation of (η^4 -diene)Ru(CO)₃ precursors
for photo-assisted chemical vapour deposition



- 4 **C P Souza** and F Fantuzzi, “Condensed-phase effects in the vacuum-ultraviolet spectra of H₂O and O₂ interstellar ice analogues”, *EPJ Web Conf*, 2026, **382**, 05003, DOI: 10.1051/epjconf/202638205003

EPJ Web of Conferences **382**, 05003 (2026)
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<https://doi.org/10.1051/epjconf/202638205003>

Condensed-phase effects in the vacuum-ultraviolet spectra of H₂O and O₂ interstellar ice analogues

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²HUN-REN Institute for Nuclear Research (Atomki), Debrecen H-4026, Hungary

Abstract. Vacuum-ultraviolet spectroscopy provides access to electronic transitions in astrophysical ices that are difficult to investigate using infrared measurements alone. Interpretation of these spectra is challenging because condensed-phase excitations may extend over several molecules and can differ substantially from the corresponding gas-phase transitions. Here, time-dependent density functional theory calculations are used to examine condensed-phase effects in molecular models of H₂O and O₂ ices. For H₂O, increasing the cluster size produces a progressive hypsochromic shift of the first intense absorption and reveals substantial mixing among diffuse virtual orbitals. For crystalline α -O₂, the calculations identify a lower-energy excitation with substantial intermolecular charge-transfer character, promoted by the or-

C.2 OTHER PUBLICATIONS

- 1 Í A O Bozzi, L A Machado, E B T Diogo, F G Delolo, L O F Barros, G A P Graça, M H Araujo, F T Martins, L F Pedrosa, L C da Luz, E S Moraes, F S Rodembusch, J S F Guimarães, A G Oliveira, S H Röttger, D B Werz, **C P Souza**, F Fantuzzi, J Han, T B Marder, H Braunschweig and E N da Silva Júnior, “Electrochemical Diselenation of BODIPY Fluorophores for Bioimaging Applications and Sensitization of ¹O₂”, *Chem Eur J*, 2024, **30**, e202303883, DOI: 10.1002/chem.202303883



Chemistry—A European Journal

Research Article
doi.org/10.1002/chem.202303883



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Electrochemical Diselenation of BODIPY Fluorophores for Bioimaging Applications and Sensitization of ¹O₂

Ícaro A. O. Bozzi^{+, [a]}, Luana A. Machado^{+, [a, i]}, Emílly B. T. Diogo^[a], Fábio G. Delolo^[a], Luíza O. F. Barros^[a], Gabriela A. P. Graça^[a], Maria H. Araujo^[a], Felipe T. Martins^[b], Leandro F. Pedrosa^[c], Lilian C. da Luz^[d], Emmanuel S. Moraes^[e], Fabiano S. Rodembusch^[d], João S. F. Guimarães^[f], André G. Oliveira^[f], Sebastian H. Röttger^[g], Daniel B. Werz^[g], Cauê P. Souza^[h], Felipe Fantuzzi^[h], Jianhua Han^[i], Todd B. Marder^[i], Holger Braunschweig^{*, [i]} and Eufrânio N. da Silva Júnior^{*, [a]}

We report a rapid, efficient, and scope-extensive approach for the late-stage electrochemical diselenation of BODIPYs. Photophysical analyses reveal red-shifted absorption – corroborated by TD-DFT and DLPNO-STEOM-CCSD computations – and color-tunable emission with large Stokes shifts in the selenium-containing derivatives compared to their precursors. In addition, due to the presence of the heavy Se atoms, competitive ISC generates triplet states which sensitize ¹O₂ and display

phosphorescence in PMMA films at RT and in a frozen glass matrix at 77 K. Importantly, the selenium-containing BODIPYs demonstrate the ability to selectively stain lipid droplets, exhibiting distinct fluorescence in both green and red channels. This work highlights the potential of electrochemistry as an efficient method for synthesizing unique emission-tunable fluorophores with broad-ranging applications in bioimaging and related fields.

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- 2 V S A Bonfim, C P Souza, D A B de Oliveira, L Baptista, A C F Santos and F Fantuzzi, ^o “Deciphering the irradiation induced fragmentation–rearrangement mechanisms in valence ionized $\text{CF}_3\text{CH}_2\text{F}$ ”, *J Chem Phys*, 2024, **160**, 124308, DOI: 10.1063/5.0188201

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Deciphering the irradiation induced fragmentation–rearrangement mechanisms in valence ionized $\text{CF}_3\text{CH}_2\text{F}$

Cite as: *J. Chem. Phys.* **160**, 124308 (2024); doi: 10.1063/5.0188201

Submitted: 20 November 2023 • Accepted: 27 February 2024 •

Published Online: 25 March 2024



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Note: This paper is part of the 2024 JCP Emerging Investigators Special Collection.

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- 3 J C de Oliveira, B U Abreu, E R S Paz, R G Almeida, J Honorato, **C P Souza**, F Fantuzzi, V F S Ramos, R F S Menna-Barreto, M H Araujo, G A M Jardim and E N da Silva Júnior, “SuFEx-Functionalized Quinones via Ruthenium-Catalyzed C–H Alkenylation: A Potential Building Block for Bioactivity Valorization”, *Chem Asian J*, 2024, **19**, e202400757, DOI: 10.1002/asia.202400757



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SuFEx-Functionalized Quinones via Ruthenium-Catalyzed C–H Alkenylation: A Potential Building Block for Bioactivity Valorization

Joyce C. de Oliveira,^[a] Breno U. Abreu,^[a] Esther R. S. Paz,^[a] Renata G. Almeida,^[a] João Honorato,^[b] Cauê P. Souza,^[c] Felipe Fantuzzi,^[c] Victor F. S. Ramos,^[d] Rubem F. S. Menna-Barreto,^[d] Maria H. Araujo,^[a] Guilherme A. M. Jardim,^{*,[a]} and Eufânio N. da Silva Júnior^{*,[a]}

Herein, we describe the Ru-catalyzed C–H alkenylation of 1,4-naphthoquinones (1,4-NQs), resulting in 1,4-naphthoquinoidal/SuFEx hybrids with moderate to good yields. This method provides a novel route for direct access to ethenesulfonyl-fluorinated quinone structures. We conducted mechanistic

studies to gain an in-depth understanding of the elementary steps of the reaction. Additionally, we evaluated the prototypes against trypomastigote forms of *T. cruzi*, leading to the identification of compounds with potent trypanocidal activity.

Introduction

Quinones are omnipresent motifs found in a wide range of living organisms,^[1] existing in nature as fundamental structures that play key roles as organic redox molecules involved in energy transduction and storage in biological systems.^[2] Quinones are also fundamental in proton-coupled electron transfer processes, such as photosynthesis^[3] and animal respiration.^[4] In the human body, quinones are vital for sustaining life, acting in blood coagulation and bone formation.^[5] It is considered one of the main groups of

and orthogonal methodologies.^[12] Since its creation in 2001 by Sharpless and Meldal,^[13] this concept permeated various scientific fields, revolutionizing research, and societal applications. It culminated in the 2022 Nobel Prize, awarded to Sharpless, Meldal, and Bertozzi for their contributions to click and biorthogonal chemistry methodologies.^[14] Within this philosophy, sulfur(VI) fluoride exchange (SuFEx) is coined as a new generation of powerful click reactions, enabling the synthesis of hypervalent sulfur compound under metal-free conditions.^[15] Since its creation in 2014, SuFEx has been considered a new embodiment of ideal click chemistry.

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- 4 Y He, C P Souza, J Weiser, M Dietz, I Krummenacher, R D Dewhurst, H Braunschweig, F Fantuzzi and J Cui, "Single-Electron Oxidation, Chloride Abstraction, and Hydride-Induced Decomposition of a Dichloro-Bis(Germylene)", *Eur J Inorg Chem*, 2024, **27**, e202400422, DOI: 10.1002/ejic.202400422



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Single-Electron Oxidation, Chloride Abstraction, and Hydride-Induced Decomposition of a Dichloro-Bis(Germylene)

Yiyi He,^[a] Cauê P. Souza,^[b] Jonas Weiser,^[c] Maximilian Dietz,^[d, e] Ivo Krummenacher,^[d, e] Rian D. Dewhurst,^[d, e] Holger Braunschweig,^{*,[d, e]} Felipe Fantuzzi,^{*,[b]} and Jingjing Cui^{*,[a]}

In this work we explore the reactivity of a dichloro-bis(germylene) compound that features a naphthyridine diimine (NDI) ligand, denoted NDI-Ge₂Cl₂. Upon reaction with the oxidant [Cp₂Fe][BAR^f₄] (Cp = C₅H₅, BAR^f₄ = [(3,5-(CF₃)₂C₆H₃)₄B]), we observed the formation of the radical species [NDI-Ge₂Cl₂]^{•+}

[BAR^f₄]⁻. Furthermore, the introduction of Na[BAR^f₄] induced a single chloride anion abstraction process, resulting in the formation of [NDI-Ge₂Cl][BAR^f₄]. The addition of Li[HB(^tBu)₃] to NDI-Ge₂Cl₂ led to the generation of NDI-Ge, presumably via a Cl/H exchange pathway followed by a decomposition process.

Introduction

Germynes, heavier analogs of carbenes, exhibit diverse reactivities, including oxidation, reduction, coordination to Lewis acids or bases, and activation of small molecules.^[1] In the case of germynes featuring a Ge–X (X = halogen) bond, further derivations, such as nucleophilic substitution, halogen extraction, and halogen/H exchange, become conceivable.^[1a,2]

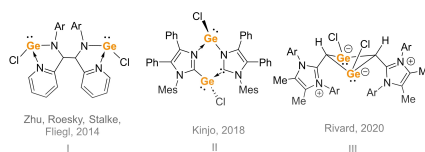


Figure 1. Structurally characterized dihalo-digermylenes (Ar = 2,6-diisopro-

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- 5 D Das, A Roy, **C P Souza**, S Mondal, S Sutradhar, P Sarkar, F Fantuzzi and B N Ghosh, “A copper complex receptor for nanomolar sulfide sensing and applications in DNA/BSA binding”, *J Photochem Photobiol A*, 2025, **461**, 116154, DOI: 10.1016/j.jphotochem.2024.116154

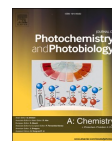
Journal of Photochemistry & Photobiology, A: Chemistry 461 (2025) 116154



Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, A: Chemistry

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A copper complex receptor for nanomolar sulfide sensing and applications in DNA/BSA binding

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ARTICLE INFO

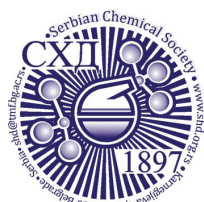
Keywords:

Sulfide sensing
Colorimetric sensors
Real-time detection
DFT calculations
Molecular docking

ABSTRACT

Traditionally toxic sulfide species (S^{2-} , HS^- , and H_2S) play indispensable roles in various biological, environmental, and industrial processes. However, excessive exposure to these species can result in numerous chronic diseases. Considering the importance of sulfide recognition, we have synthesized and characterized a simple 1:1 Cu(II) complex of L ($CuCl_2L$ receptor) based on a substituted 2,6-dipyrazinylpyridine (dppy) moiety (L = 4-(2,6-di(pyrazin-2-yl)pyridin-4-yl)-N,N-dimethylaniline). The complex was analyzed both experimentally and computationally using DFT and TD-DFT calculations. The *in-situ* prepared $CuCl_2L$ receptor is employed to selectively recognize sulfide species (detection limit: 82.50 nM) in the presence of other anions in higher concentration (ten equivalents of F^- , Cl^- , Br^- , I^- , $CH_3CO_2^-$, HCO_3^- , $H_2PO_4^-$, NO_3^- , SO_4^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, CO_3^{2-} , and HPO_4^{2-} (10 mM)) in aqueous acetonitrile (2:1 v/v, 10 mM HEPES buffer, pH 7.4) through absorption spectral studies.

- 6 F Fantuzzi, J B Maljković, M Zlatar, **C P Souza**, H M Quitián-Lara, P Nag, B Antony, B P Marinković and N J Mason, “Centennial of quantum theory in Belgrade: CEQPAS and the molecular excited state spectroscopy (MOLESs) initiative”, *J Serb Chem Soc*, 2025, **90**, 1553–1561, DOI: 10.2298/JSC251118083F



J. Serb. Chem. Soc. 90 (12) 1553–1561 (2025)
JSCS-5472

Journal of the Serbian
Chemical Society

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Letters to Editor

Published 26 December 2025

LETTER TO THE EDITOR

Centennial of quantum theory in Belgrade: CEQPAS and the molecular excited state spectroscopy (MOLESs) initiative

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- 7 E R S Paz, **C P Souza**, J C de Oliveira, R G Almeida, C Herrera-Acevedo, S Lakoh, G A M Jardim, E N da Silva Júnior and F Fantuzzi, “Ruthenium-Catalyzed C–H Alkenylation of Trypanocidal Naphthoquinones: A Mechanistic Benchmarking Study”, *ChemistryOpen*, 2026, **15**, e202500465, DOI: 10.1002/open.202500465



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doi.org/10.1002/open.202500465



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Ruthenium-Catalyzed C–H Alkenylation of Trypanocidal Naphthoquinones: A Mechanistic Benchmarking Study

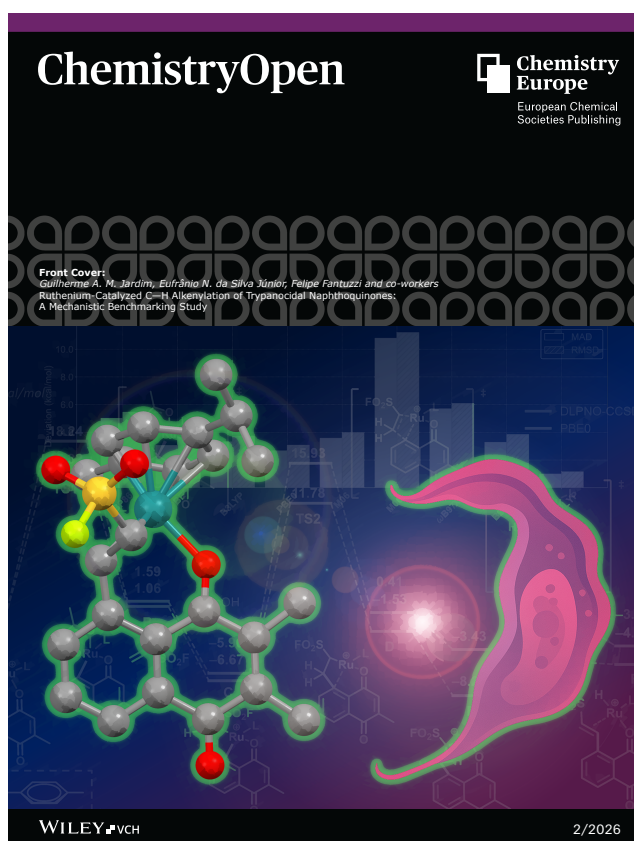
Esther R. S. Paz, Cauê P. Souza, Joyce C. De Oliveira, Renata G. Almeida, Chonny Herrera-Acevedo, Sulaiman Lakoh, Guilherme A. M. Jardim,* Eufânio N. da Silva Júnior,* and Felipe Fantuzzi*

Dedicated to Professor Marco A. C. Nascimento on the occasion of his 78th birthday

Quinones are privileged scaffolds in biological redox chemistry and drug discovery, but methods to install versatile click handles onto their cores remain scarce. This work presents a comprehensive computational study of the Ru(II)-catalyzed C–H alkenylation of menadione with ethenesulfonyl fluoride, a transformation that introduces sulfonyl-fluoride groups for subsequent SuFEx chemistry. Nine density functionals—from GGAs to double hybrids—are first benchmarked against DLPNO-CCSD(T) reference energies for all key on-cycle intermediates and transition states along the cationic $[\text{Ru}(\text{OAc})(p\text{-cymene})]^+$ pathway. Among them, ωB2PLYP best matches the coupled-cluster reference and is the only method to achieve root-mean-square deviations of $\approx 1 \text{ kcal mol}^{-1}$. Given that

the computed on-cycle barriers are modest, the results indirectly support that the overall rate is dictated by off-cycle formation of the active cationic species via ligand exchange/speciation. Within the catalytic cycle, C–H activation presents the highest global barrier, although migratory insertion can display a higher local barrier (relative to its immediate precursor) for specific ring substitutions. Finally, it is shown that the $\text{r}^2\text{SCAN-3c}$ composite method offers a computationally efficient route for probing analogous catalytic cycles. These results deliver a robust protocol for designing naphthoquinone derivatives as next-generation therapeutic agents against *Trypanosoma cruzi* and related parasites.

Cover feature:



- 8 A Marulanda-Gallego, C P Souza and F Fantuzzi, “Local structural effects on the VUV absorption of H₂S ice models: A TD-DFT cluster investigation”, *EPJ Web Conf*, 2026, **382**, 05002, DOI: 10.1051/epjconf/202638205002

EPJ Web of Conferences **382**, 05002 (2026)
1st RAP 2026

<https://doi.org/10.1051/epjconf/202638205002>

Local structural effects on the VUV absorption of H₂S ice models: a TD-DFT cluster investigation

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Abstract. Interstellar ice mantles on dust grains play a central role in astrochemical processes and in the formation of complex organic molecules. Hydrogen sulphide (H₂S) is considered a potential sulphur reservoir in these ices, yet it has not been conclusively detected in the solid phase, an absence that has been associated with the sulphur depletion problem. In this work, time-dependent density functional theory (TD-DFT) calculations were employed to simulate the vacuum ultraviolet (VUV) absorption spectra of small H₂S clusters as models of amorphous-like and crystal-derived interstellar-ice analogues. The

- 9 K Cielinska, A V Verkhovtsev, C P Souza, M D Dickens, A V Solov'yov, N J Mason and F Fantuzzi, “Unpassivated edges as gateways to collision-driven topological transformations in finite graphene nanoflakes”, *The European Physical Journal D*, 2026, **80**, 134, DOI: 10.1140/epjd/s10053-026-01242-8

Eur. Phys. J. D (2026)80:134
<https://doi.org/10.1140/epjd/s10053-026-01242-8>

THE EUROPEAN
PHYSICAL JOURNAL D



Research - Atoms, Molecules, Ions, and Clusters

Unpassivated edges as gateways to collision-driven topological transformations in finite graphene nanoflakes

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Received 29 April 2026 / Accepted 3 August 2026
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Abstract. Finite graphene nanoflakes occupy a unique position in the carbon allotrope landscape. Near equilibrium, these systems exhibit pronounced structural robustness, indicating that large-scale allotropic transformations require strongly non-equilibrium energy deposition. In this work, we investigate how unpassivated graphene edges act as chemically active gateways for collision-driven topological transformations in finite graphene systems. Using reactive molecular dynamics simulations, we model energetic collisions involving a C₆₀ fullerene projectile and a finite C₂₉₆ graphene nanoflake across a broad parameter space of collision energies, incidence angles, and edge orientations. The structural response is analysed through statistical transformation maps that quantify the probability of nanoflake bending, edge stitching, and the formation of nanotube-like structures. We identify a regime of collision energies and oblique incidence angles under which localised energy deposition at unpassivated edges promotes bond rearrangement, cooperative bending, and covalent stitching between opposing edges. Furthermore, we find that armchair-directed impacts align opposing zigzag edges and promote efficient edge-to-edge stitching over a broader parameter range. In contrast, zigzag-directed impacts are associated with a higher probability for atom

- 10 A T Muiña, L E Borchert, Z Kaňuchová, D V Mifsud, **C P Souza**, A M Wilson, A T Hopkinson, M Mikkelsen, J Zhang, J C Santos, J G M Schrauwen, D Ramsamoedj, M Minissale, E Salomon, M Accolla, H Linnartz, B Redlich, M Zlatar, A Dawes, N J Mason, G Strazzulla, N C Jones, S V Hoffmann, L Hornekær, A M Cassidy, M S Gudipati, T Hempel, F Fantuzzi and S Ioppolo, “Survey of the Vacuum-Ultraviolet Spectroscopy and Absorption Cross-Sections of Astrophysical Ice Analogs: A Combined Experimental and Theoretical Study”, Unpublished draft manuscript, 2026

C.3 ORAL PRESENTATIONS IN CONFERENCES

- 1 “Updates on Alkanethiol SAMs Simulation”, *MultiChem Summer School on theoretical and computational methods for studying irradiation-driven physics and chemistry processes*, Bad Bertrich, Germany. 7 August **2023**.
- 2 “Multiscale Simulation of Photoassisted Chemical Vapour Deposition”, *The Eight International Conference Dynamics of Systems on the Nanoscale and The Third Annual Conference of the COST Action Multiscale Irradiation and Chemistry Driven Processes and Related Technologies (DySoN-MultiChem)*, Tbilisi, Georgia. 11 April **2024**.
- 3 “A Tale of Two Molecules” or “Metal Deposition at Room Temperature: Theoretical investigation of precursors for photoassisted chemical vapour deposition”, *The 2024 Collisions Physics and Chemistry and their Applications Conference and A Workshop of the COST Action Multiscale Irradiation and Chemistry Driven Processes and Related Technologies (COPCA-MultiChem)*, Valletta, Malta. 15 October **2024**.
- 4 “Alkanethiol SAMs on Gold: Assessment of force field parameters”, *The 12th International Symposium Atomic Cluster Collisions and The Final Conference of the COST Action Multiscale Irradiation and Chemistry Driven Processes and Related Technologies (ISACC-MultiChem)*, Heidelberg, Germany. 17 July **2025**.
- 5 “Computational Simulation of VUV Absorption Spectra of Astrochemical Ices”, *Centennial of Quantum Theory: Progress in Atomic and Molecular Structure (CEQPAS)*, Belgrade, Serbia. 4 November **2025**.
- 6 “Computational Simulation of VUV Absorption Spectra of Astrochemical Ices”, *1st Roundtable on Astroscience and Planetary Analogues (RAP)*, Dhariyawad, India. 9 January **2026**.
- 7 “Excited-state Dissociation of (η^4 -diene)Ru(CO)₃ Precursors for Photoassisted Chemical Vapour Deposition”, *Workshop of the COST Innovators Grant Innovative Digital Control for 3D Nanoprinting (INDICO)*, Frankfurt, Germany. 19 February **2026**.
- 8 “Multiscale Simulation of Photoassisted Chemical Vapour Deposition”, *49th International Congress of Theoretical Chemists of Latin Expression (QUITEL)*, Coimbra, Portugal. 7 July **2026**.
- 9 “Multiscale Simulation of Photoassisted Chemical Vapour Deposition”, *MBN Science Forum 2026*, Oldenburg, Germany. 31 August **2026**.