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"Simulating Laser-Induced Dynamics in Next Generation Photo-Acid Materials for EUVL"

Description of aim(s)

Lithography is an extremely important step in the process of manufacturing computer chips, Extreme Ultra-Violet Lithography (EUVL) can be used to engrave patterns onto computer chips using 13.5nm photons, this allows for extremely fine minute patterns to be produced on each computer chip and can make computer chips more efficient. The goal of this fourth year project is to determine the suitability of potential EUVL resists by simulating their behaviour to being excited by a laser and collecting the information about the electronic structure of the molecule that this gives us, this is achieved using a quantum chemistry programme known as ORCA. ORCA performs *"Ab Initio"* calculations or "first principal" calculations, strictly relying on physical constants and approximations (such as the Born-Oppenheimer approximation) to produce results which closely emulate what can be achieved by performing Transient Absorption Spectroscopy (TAS) in a laboratory. The overall goal of the project is to be able to produce UV/VIS and emission spectra of multiple different molecules which can then be used to determine the steady state electronic structure of the molecule and then find the excited state electron density and decomposition process.

Progress to date

The project began by performing basic calculations on diatomic molecules such as H_2, N_2 and Cl_2 as well as a H_2O molecule to determine the vibrational frequencies which represent the bending and stretching of the molecules as well as generating an IR spectrum as well as calculating the bond length and comparing them to values found in the literature.

Since then we have moved on to much larger and more complex molecules such as Pyrene ($C_{16}H_{10}$), Tris(bipyridine)ruthenium(II) chloride ($C_{30}H_{24}N_6Cl_2Ru{\cdot}6H_2O$) and (bipyridine)Ruthenium Acetylacetone. ($C_{30}H_{24}N_6Cl_2Ru{\cdot}H_2O$) and also started doing comparison of the UV/VIS Spectra in different solvents such as water, acetone, acetonitrile and methanol. Below I have included example graphs of the UV/VIS spectrum of Tris(bipyridine)ruthenium(II) chloride and the molecule Pyrene compared to a comparable UV/VIS spectrum found in the literature.

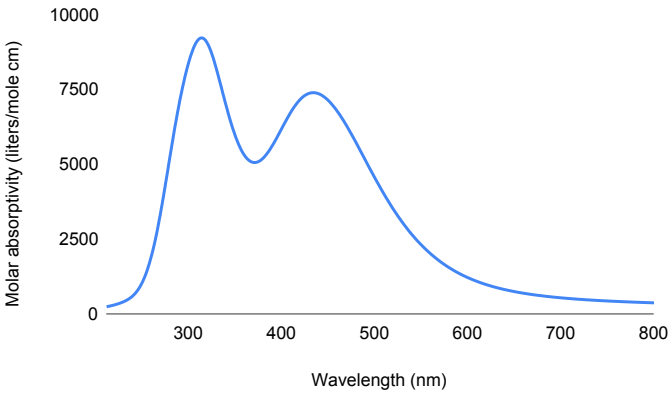

Figure 1: UV/VIS spectrum of Tris(bipyridine)ruthenium(II) chloride

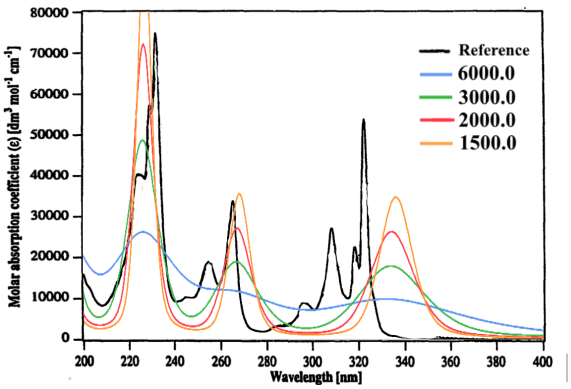

Figure 2: Pyrene UV/VIS compared to spectrum found in Andreas Thony & Michel J, Rossi paper[1] for different values of FWHM in cm^{-1}

This data was generated using Gaussian 16 an electronic structure program used by both chemists and physicists for its wide-ranging suite of advanced modelling capabilities[2]. The computation process was all carried out at the Irish Centre for High-End Computing (ICHEC) on the primary high-performance computer Kay[3].

Reviewing the literature around Pyrene we were able to compare our UV/VIS spectrum with previously published papers[1][4][5] and determine which transitions were responsible for each absorption peak, unfortunately we were unable to get the absorption peak for pyrene in the visible spectrum at 480nm which should be visible in Pyrene in liquid phase as this absorption peak is due to an excited dimer which comes about when multiple Pyrene molecules interact with each other. We believe this is due to the fact that our current model only account for a single Pyrene molecule and so we have begun the process of working towards the affects of pi stacking on the Pyrene UV/VIS spectrum as we also move on to working on Ruthenium molecules.

Substantial progress has also been made in understanding the underlying theory behind Quantum Chemistry, including solving The Schrödinger Equation for The Hydrogen Atom, learning about Frontier Molecular Orbital Theory and Point Group Theory.

Future aim(s)

Our current aim is to continue simulating molecules in solvents which we can reasonably replicate in the laboratory and compare the quantum chemistry prediction with real world measurements we have taken ourselves. Once our predictions have been verified and backed up by performing TAS we can begin making qualitative statements about the suitability of these materials as EUVL resists in the future.

References

[1] Andreas Thony, Michel J. Rossi, "Gas-phase UV spectroscopy of anthracene, xanthone, pyrene, 1-bromopyrene and 1,2,4-trichlorobenzene at elevated temperatures" Journal of Photochemistry and Photobiology A: Chemistry, Volume 104, Issues 1-3, 1997, Pages 25-33, ISSN 1010-6030 https://doi.org/10.1016/S1010-6030(96)04575-3

[2] Gaussian (2017) "About Gaussian 16" https://gaussian.com/g16main/

[3] ICHEC (2018) "Kay — ICHEC - Irish Centre for High-End Computing" https://www.ichec.ie/about/infrastructure/kay

[4] Colleen M. Jones and Sanford A. Asher, "Ultraviolet resonance Raman study of the pyrene S_4, S_3, and S_2 excited states". J. Chem. Phys. 89, 2649-2661 (1988) https://doi.org/10.1063/1.455015

[5] Nicolas P.E. Barry, Bruno Therrien, "Chapter 13 - Pyrene: The Guest of Honor", Organic Nanoreactors, Academic Press (2016), Pages 421-461, ISBN 9780128017135, https://doi.org/10.1016/B978-0-12-801713-5.00013-6.