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X-RAY ABSORPTION CALCULATIONS OF GROUND STATE AND ELECTRONIC TRANSITIONS FOR MOLECULES AND CRYSTALS OF ACRIDINE

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Acridine crystal's spectral characteristics and structure were obtained using density functional theory (DFT) calculations. The x-ray absorption spectroscopy (XAS) and UV-Vis (ultraviolet-visible) absorption spectra approaches were used to determine. The absorption coefficient at the different wavelengths and energies in acridine moleculae. We examined the possible results using the x-ray absorption of acridine to investigate the quantum coherence as well as correlations of the electronic transition from HOMO to LUMO with an energy gap of +6.6646 eV. Our calculations are in agreement with the experiments.retarding compositions are safe in production and at all stages of circulation.

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1. Introduction

The performance of organic molecules' theoretical calculation of optical properties has remained a challenging endeavor. Here, we present a comparative theoretical/ experimental investigation on acridine molecule spectra on the basis of DFT or density functional theory [1, 2, 3]. UV-Vis (ultraviolet-visible) techniques and X-ray absorption spectroscopy (XAS) that are primarily used to characterize acridine molecule in various forms such as liquid, bulk, nanoscale or solid motivated this investigation [4]. Meanwhile acridine's spectroscopic attributes are pivotal to comprehend how the acridine system and the polymer behaves [5, 6, 3].

X-ray spectra (XAS) is an experimental technique for investigating local surface interactions of molecules, i.e., a tool to measure the x-ray absorption coefficient's energy-dependent fine structure in close proximity to a particular element's absorption edge. This technique is especially useful when it comes to evaluating low Z atom systems, such as organic molecules [7-11].

For several years, analog- acridine synthesis has elicited has elicited interest in the field of chemistry (medicinal and organic), since the heterocyclic nucleus is associated with many sources [1]. Acridine refers to a compound with the formula C13H9N. This organic compound is an alkaloid from anthracene with a central CH group replaced by nitrogen (Fig. 1). Acridine is known to get crystalized in light yellow/colorless needless with 346℃ as the boiling point and 110℃ being the melting point. It can cause skin irritation and is associated with blue fluorescence denoted by salt solutions [1].

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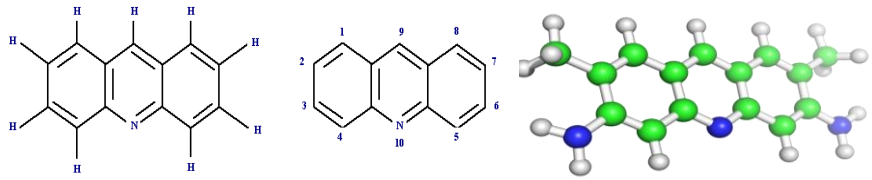

Fig.1 Acridine chemical structure

The x-ray spectroscopy and UV-Vis spectra techniques were utilized for obtaining the absorption coefficient, molecular structure, lower unoccupied molecular orbital (LUMO), circular dichroism spectrum (CDS), high occupied molecular orbital(HOMO), and magnitude of refractive index [12]. These increasingly popular are being used to measure the samples' linear or nonlinear extinction coefficient and MO. It has many advantages such as simplicity, high sensitivity, quick and other advantages [7, 13]. This work aimed to examine the acridine's optical properties and fluorescence spectra at varied energy (100-1000 eV) and wavelength at (100-1000 nm). We compared the x-ray absorption calculations with those of UV-Vis spectra [14, 15].

2. Theoretical description (dipole approximation)

Quantum mechanical perturbation theory stated that the rate of transition between level of the core and the state attained eventually is directly correlated with the multiplication of matrix element $M's$squared modulusand the density of state ρas **[15].**

$$\mu \propto |M|^2 \rho \propto \left|\langle f|H_{if}|i\rangle\right|^2 \rho \tag{1}$$

Where,$|i\rangle$ refers to the initial state and $\langle f|$ signifies the final state. On the other hand, H_{if} denotes Hamiltonian that elucidates the how the x-ray photon's electromagnetic field interacts with the atom being absorbed. XAS examines a structure's localized rate of x-ray absorption across a spectrum of wavelengths or energies. When shined on the system, X-rays tuned to the energy of a structure's chemically inert core electrons have a high probability of absorption and excitation. Lifted from the ground state, an excited electron will leave an electron hole in its wake. When the excited state is highly unstable, the vacancy will immediately notified by another electron. The difference in energy from the excited state is mitigated by either a photon's or an electron's emission. The spectrum's magnitude is given by the probability of transition, which is approximated within Fermi's golden rule (Equation 2) [3]:

$$P_{if} = \frac{2\pi}{\hbar}|H'_{if}\ |^2 \rho_f \tag{2}$$

Where, the matrix element$H'_{kn} = \langle \Psi_k|H'|\Psi_n\rangle$ and ρ_f describes the density of final energy states. However, just one electron is supposedly involved in the rectifications owing to the sufficient addition of myriad impacts. In a static electric field, the perturbed Hamiltonian can be approximated by $H' = -\hat{\epsilon}.R$; where,$\hat{\epsilon}$ signifies the electromagnetic vector potential's polarization direction and the position operator being denoted by R denotes the position operator. Equation 3 entails the use of the approximation of an electron with the approximation of dipole:

$$\mu \propto \left|\langle f|\hat{\epsilon}.\vec{R}|i\rangle\right|^2 \rho \tag{3}$$

The approximation of dipole suffices in the majority cases; however, interactions of quadrupole could assume significance for L-edges and high Z elements. XAS ascertains the photon absorption's local rate due to core electron excitation across an energy spectrum (typically on the

order of 100-1000 eV).The rate of absorption scales with the density of possible final states, ρ_f. Transitions to some states are forbidden by dipole selection rules, thus indicating that the transition probability is nonzero if and only if the matrix element does not have odd parity (Equation 4).

$$\langle \Psi_i | H' | \Psi_f \rangle = \int_{-\infty}^{+\infty} \Psi_i^* \mu \Psi_f \, d\tau \tag{4}$$

3. Computational study

The computational method's description is included in the manuscript's main text. Berkeley XAS tool, one the open source Quantum espresso packages was utilized for accessing the accuracy of the applied computational method to investigate the absorption spectrum due to a 1*s*electron core hole (K-edge) using density functional theory (DFT)[3]. We calculated the 1*s*electron bond energy; the tool determines the relative energy shift of the K-edge with respect to an isolated atom. An overlay of two available crystal structures is shown by Equation 5.

$$EnergyShift = \left(E_{system,x} - E_{system,gs}\right) - \left(E_{atom,x} - E_{atom,gs}\right) - E_{LUMO} \tag{5}$$

Where, x denotes an excited state, gsrefers to the energy of the ground-state, and *LUMO* signifies the lowest unoccupied molecular orbital. Berkeley XAS then applies a final shift in addition to the calculated shift in Equation 5. The final shift is independent of molecular structure and gets approximated by fitting peak energy with experimental data from the Hitchcock Group at McMaster University. Berkeley XAS considers a rigid molecule when calculating spectra, but, this is not a realistic picture. Excited states are known to have short lifetimes and molecules at finite temperature will distort and break bonds, leading to peak broadening and shifting. Using fast measurements, these differences can be alleviated computationally through molecular dynamics or experimentally. Furthermore, calculated peak widths are expected to be narrower than experiment due to underestimation of band-width within DFT [13].

4. Results and Discussions

4.1. X-ray absorption

Figs.2 and 3 show the computed x-ray spectra for acridine from the electronic transitions method are shown. The acridine spectra were simulated using the Berkeley XAS software in the nano HUB tools [16]. Berkeley XAS evaluates the absorption spectrum due to a 1selectron core hole (K-edge) using density functional theory.

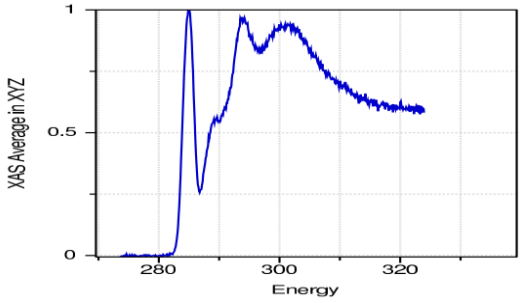

Fig2.XAS spectra of acridine as function of energy using excited carbon atom

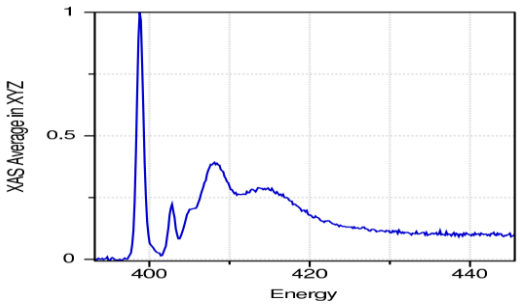

Fig.3. XAS spectra of acridine as function of energy using excited nitrogen atom

Berkeley XAS subsequently implements a final shift atop the calculated shift in Equation 5. Figure 2 shows that a final energy shifts its +285.44 eV for the carbon atom excited and +396.23 eV when a nitrogen atom is excited. Notably, this final ship does not depend on the molecular structure and was approximated by the fitting peak energy with experimental data provided by the Hitchcock Group at McMaster University [15]. The spectra utilized for the purpose of peak fitting were pyridine, carbon dioxide, and ethanol, all of which are available from the dropdown on the molecule structure input page. While Berkeley XAS spectra are also renormalized to a maximum height of 1, the calculated absolute values of the peak heights are not importance. Therefore, only their relative heights need to be examined. Since bonding mostly depends on valence electrons, the nucleus as well as remaining electrons (core electrons) are simplified into a single effective potential, referred to as pseudopotential.

4.2. UV-VIS spectra

UV-Vis absorption spectra were obtained for acridine [14]; Figure 4 shows the behavior. UV-Vis spectra calculates the molecular electronic structures of acridine using the SCF-MO package ORCA. CI-singles (CIS) are used to calculate states that are excited with Hamiltonian ZINDO (semi empirical). Figures 4, 5, and 6 illustrate the absorption spectrum and MO.

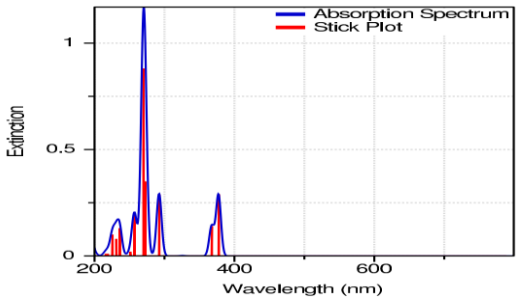

Fig.4. UV-Vis spectra of acridine as function of wavelength; blue line represent the absorption spectrum and red line is the stick plot

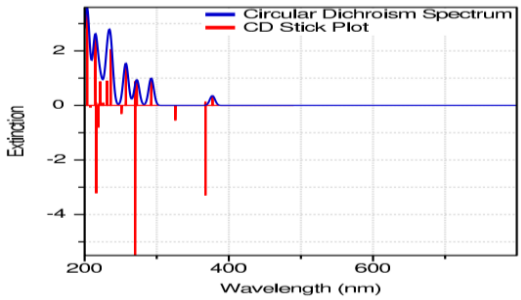

Fig.5. UV-Vis spectra of acridine as function of wavelength; blue line represent the circular dichroism spectrum and red line is the CD stick plot.

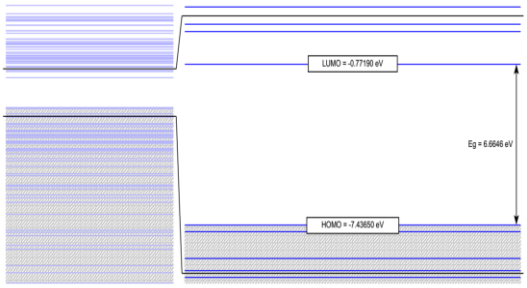

Fig.6. MO diagram of acridine molecular orbital energies; where, LUMO = -0.77190eV, HOMO=-7.43650eV and energy gap E_g =6.6646 eV

4. Conclusion

This study examined the spectral characteristics, obtaining the structure of acridine crystal using DFT calculations. X-ray absorption spectroscopy (XAS) was used to determine the x-ray spectra of acridine from DFT approaches; the computed maximum absorption scaled by energies +285.44 and +396.23 eV for the carbon and nitrogen atoms excited, respectively UV-Vis spectra measured the maximum absorption of 1.2 at the approximate wavelength at 290nm. According to our calculations, the maximum absorption of acridine is attributed to the electronic transition from HOMO to LUMO.

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References

[1]. R. Kumar, M. Kaur, M. Kumari, Acridine: A Versatile Heterocyclic Nucleus. Drug Research **69**(1),3(2012).
[2]. S. G. Urquhart, U. Lanke, J. Fu, Int. J. Nanotech. **5**, 1138 (2007).
[3]. C. S. Schnohr, M. C. Ridgway, X-Ray Absorption Spectroscopy of Semiconductors, Springer (2014).
[4]. B. Kaulich, P. Thibault, A. Gianoncelli1, M. Kiskinova, J. Phys.: Condens. Matter **23,**083002 (2011)
[5]. E. Bauer, Surface Microscopy with Low Energy Electrons, Springer, NY (2014)

[6]. D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Principles and Applications, Cambridge University Press, (2000)
[7]. L. H. Aboud, Z. F. Mahdi, W. J. Abed AL-Zahra, Academic Research International **5**(4) (2014)
[8]. D. Sayre, H. N. Chapman, Acta Crystallographica A **51**, 237 (1995)
[9]. C. C. Sloop, H. Ade and et al., J. Polym. Sci.: Part B: Polym. Phys. **39**, 531 (2001)
[10]. H. Ade, H. Stoll, Nature Materials **8**(4), 281(2009).
[11] M. K. Armbruster, B. Schimmelpfennig, et al., J. El. Spectrosc. Rel. Phen. **169**,51 (2009).
[12]. J. E. Ehrlich, X. L. Wu, Lee, et al., Optics Letters **22**(24), 1843(1997).
[13]. A. M. Bradshaw, J. Somers, Physica Scripta, **T31**, 189(1998).
[14]. B. Tejerina, "UV/Vis Spectra simulate, (2014)
[15]. B. Han, A. Taber, K. Gilmore, and D. Prendergast, Berkeley XAS (2016).
[16]. B.A. Collins, J. E. Cochran, et al., Nature Materials **11**, 536(2012).