

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

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The spectral characteristics and structure of acridine crystal were obtained using density functional theory (DFT) calculations. The absorption coefficient at the different wavelengths and energies in acridine molecule were determined using the x-ray absorption spectroscopy (XAS) and UV-Vis (ultraviolet-visible) absorption spectra approaches. We discussed the possible results using the x-ray absorption of acridine to probe the quantum coherence and correlations of the electronic transition from HOMO to LUMO with energy gap +6.6646 eV. Our calculations are in agreement with the experiments.

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### 1. Introduction

The performance of theoretical calculation of optical properties of organic molecules has been a major challenge for many years. Here, we present a comparative experimental and theoretical investigation on acridine molecule spectra based on density functional theory (DFT)[1,2,3]. The investigation was motivated by x-ray absorption spectroscopy (XAS) and UV-Vis (ultraviolet-visible) spectra techniques used extensively for the characterization of acridine molecule in solid or liquid, crystalline or amorphous, bulk or nanoscale form[4]. On the other hand, the spectroscopic properties of acridine are fundamentally important to understanding the behavior of acridine system and by extension, the polymer itself [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 energy-dependent fine structure of the x-ray absorption coefficient near the absorption edge of a particular element. This technique is particularly useful for examining systems with low  $Z$  atoms, such as organic molecules[7-11].

The synthesis of acridine and analogs has attracted considerable attention from organic and medicinal chemistry for many years, as a number of natural sources have been reported to have this heterocyclic nucleus[1]. Acridine, an organic compound with the formula  $C_{13}H_9N$ , is an alkaloid from anthracene with one of the central  $CH$  groups replaced by nitrogen (Fig. 1). It crystallizes in colorless to light yellow needles with a melting point of 110°C and boiling point of 346°C. It is characterized by its irritating action on skin and by the blue fluorescence showed by solutions of its salts [1].

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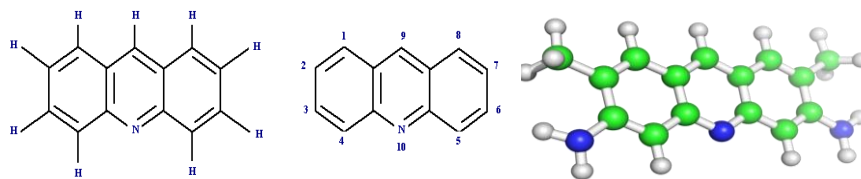


Fig.1. Acridine chemical structure

The x-ray spectroscopy and UV-Vis spectra techniques were used to obtain the molecular structure, absorption coefficient, circular dichroism spectrum (CDS), lower unoccupied molecular orbital (LUMO), high occupied molecular orbital (HOMO), and magnitude of refractive index [12]. These techniques are an increasingly popular, used for the measurement of linear or nonlinear extinction coefficient and MO of the samples. It has many advantages such as simplicity, high sensitivity, quick and other advantages [7,13]. The aim of this work was to study the optical properties and fluorescence spectra of acridine at different 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)

According to quantum mechanical perturbation theory, the transition rate between the core level and the final state is proportional to the product of the squared modulus of the matrix element  $M$  and the density of state  $\rho$  as given in Equation 1 [15].

$$\mu \propto |M|^2 \rho \propto |\langle f | H_{if} | i \rangle|^2 \rho \quad (1)$$

Where,  $|i\rangle$  and  $\langle f|$  denote the initial and final state, respectively, and  $H_{if}$  represents Hamiltonian, which describes the interaction of the electromagnetic field of the x-ray photon with the absorbing atom. XAS examines a structure's localized rate of x-ray absorption across a spectrum of wavelengths or energies. X-rays tuned to the energy of a structure's chemically inert core electrons have a high probability of absorption and excitation when shined on the system. An excited electron will be lifted from the ground state, leaving an electron hole in its wake. When the excited state is highly unstable and the vacancy will immediately be filled by another electron. The difference in energy from the excited state is compensated by the emission of either a photon or another electron. The magnitude of the spectrum is given by the probability of transition, which we approximate within Fermi's golden rule (Equation 2) [3]:

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

Where, the matrix element  $H'_{kn} = \langle \Psi_k | H' | \Psi_n \rangle$  and  $\rho_f$  describes the density of final energy states. Practically, however, it is usually assumed that only one electron is involved in the transition and corrections due to many-body effects added at a later stage. In a static electric field, the perturbed Hamiltonian can be approximated by  $H' = -\hat{\epsilon} \cdot R$ ; where,  $\hat{\epsilon}$  is the polarization direction of the electromagnetic vector potential and  $R$  is the position operator. Using one-electron approximation together with the dipole approximation, we get (Equation 3):

$$\mu \propto |\langle f | \hat{\epsilon} \cdot \vec{R} | i \rangle|^2 \rho \quad (3)$$

In most cases, the dipole approximation is sufficient; however, quadrupole interactions may become important for high  $Z$  elements and  $L$ -edges. X-ray absorption spectroscopy measures the local rate of photon absorption 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,  $\rho_f$ . Transitions to some states are forbidden by dipole selection rules, which indicate that transition probability is nonzero if and only if the matrix element does not have odd parity (Equation 4).

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

### 3. Computational study

The description of the computational method is included in the main text of the manuscript. Berkeley XAS tool, one the open source Quantum espresso package was used to access the accuracy of the applied computational method to examines the absorption spectrum due to a 1selectron core hole ( $K$ -edge) using density functional theory (DFT)[3]. We calculated the 1selectron bond energy; the tool determines the relative energy shift of the  $K$ -edge with respect to an isolated atom. Equation 5 shows an overlay of two available crystal structures.

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

Where,  $x$  indicates an excited state,  $gs$  refers to the energy of the ground-state, and  $LUMO$  is the lowest unoccupied molecular orbital. Berkeley XAS then applies a final shift on top of the calculated shift in Equation 5. The final shift is independent of molecular structure, and was approximated by fitting peak energy with experimental data from the Hitchcock Group at McMaster University. Berkeley XAS considers a rigid molecule in calculating spectra; however, this is not a realistic picture. Excited states have short life-times and molecules at finite temperature will distort and break bonds, resulting in peak broadening and shifting. These differences can be alleviated computationally through molecular dynamics or experimentally using fast measurements. 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

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

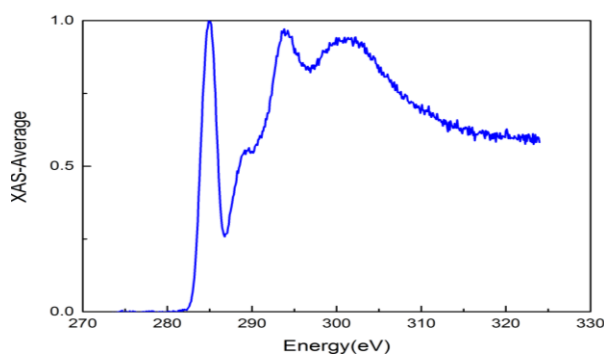


Fig2. Shown the XAS spectra of Acridine as function of energy when the carbon atom excited.

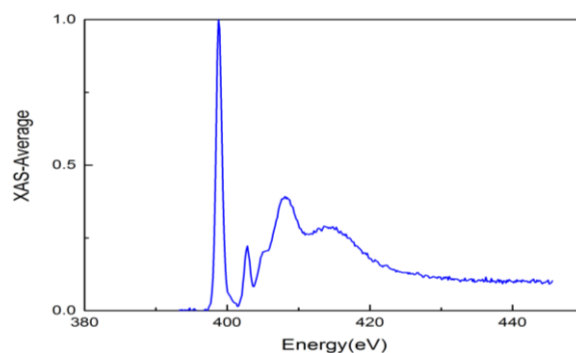


Fig.3. Shown the XAS spectra of Acridine as function of energy using excited nitrogen atom

Berkeley XAS then applies a final shift on top of the calculated shift in Equation 5. From Figure 2, a final energy shifts its +285.44 eV for the carbon atom excited and +396.23 eV when a nitrogen atom is excited. The final shift is independent of molecular structure and was approximated by fitting peak energy with experimental data from the Hitchcock Group at McMaster University [15]. The spectra used for peak fitting were carbon dioxide, ethanol, and pyridine, which are all available from the drop down on the molecule structure input page. Berkeley XAS spectra are also renormalized to a maximum height of 1, however the calculated absolute values of the peak heights are unimportant thus only their relative heights should be examined. Since bonding is mostly dependent on the valence electrons, the nucleus and remaining electrons (core electrons) are simplified into a single effective potential, called pseudopotential.

#### 4.2. UV-VIS spectra

UV-Vis absorption spectra were obtained for acridine [14]; the behavior is shown in Figure 4. UV-Vis spectra use the SCF-MO package ORCA to calculate acridine molecular electronic structures. Excited states are calculated via CI-singles (CIS) with semi empirical Hamiltonian ZINDO. The MO and absorption spectrum are displayed graphically as shown in Figs. 4, 5 and 6.

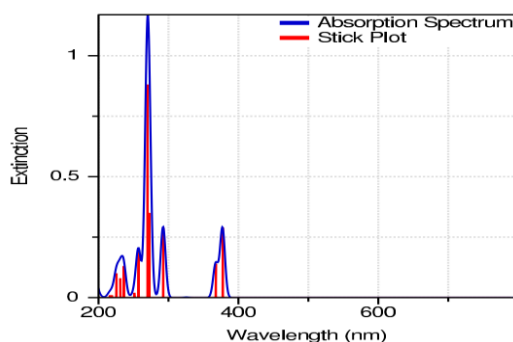


Fig.4. UV-Vis spectra of acridine as function of wavelength; blue line represent the absorption spectrum and red line is the stick plot

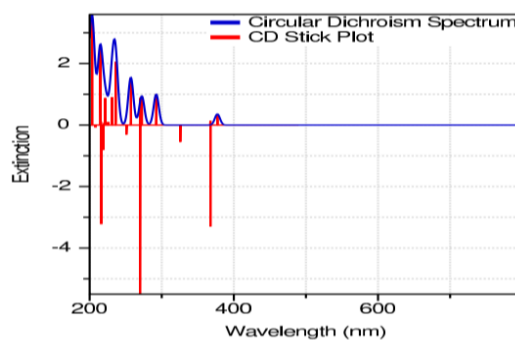


Fig.5. UV-Vis spectra of acridine as function of wavelength; blue line represent the circular dichroism spectrum and red line is the CD stick plot.

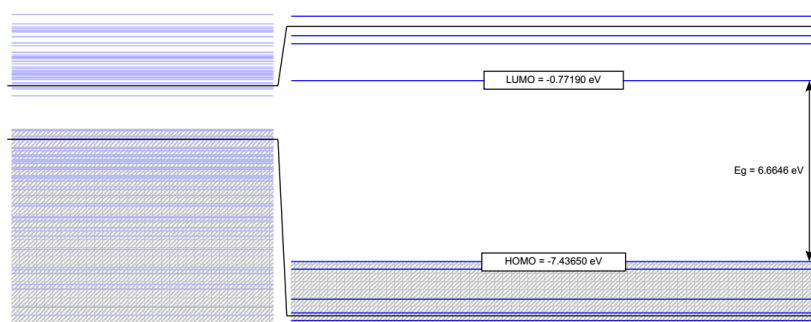


Fig.6. MO diagram of acridine molecular orbital energies; where, LUMO =  $-0.77190\text{eV}$ , HOMO =  $-7.43650\text{eV}$  and energy gap  $E_g = 6.6646\text{ eV}$

#### 4. Conclusion

We have studied the spectral characteristics, and the structure of acridine crystal was obtained using DFT calculations. The x-ray spectra of acridine from DFT approaches were determined using x-ray absorption spectroscopy (XAS); the computed maximum absorption scaled by energies  $+285.44$  and  $+396.23\text{ eV}$  for the carbon and nitrogen atoms excited, respectively. The maximum absorption of 1.2 was measured by UV-Vis spectra at the approximate wavelength at  $290\text{nm}$ . Our calculation showed that the maximum absorption of acridine is due to the electronic transition from HOMO to LUMO.

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