FLUORESCENCE DYNAMICS AND ELECTRONIC STRUCTURE STUDIES OF QUINOLINE DERIVATIVES AND APPLICATIONS

ABSTRACT

Thesis Submission for the Degree of
Doctor of Philosophy
In Physics
By
Swatantra Kumar Yadav

Supervisor
Dr. Hirdyesh Mishra

Department of Physics
Banaras Hindu University
Varanasi-221005 (U.P.), India

Enrolment No.: 341872
(August, 2017)
The electronic states and luminescence properties of quinoline and their derivatives have been the subject of considerable interest. Spectral studies of quinoline can be traced back to five or six decades. Being isoelectronic with naphthalene, these molecules provide useful comparisons for checking the electronic and vibrational state assignments, ionization potentials, and other properties of the parent hydrocarbon. In addition, these molecules possess nonbonding electrons which give rise to n–π* states whose location and characterization are of both theoretical and practical significance. Further, solvents have an important influence on the luminescence property of N-heterocyclic compounds. Quenching of fluorescence as a consequence of increased spin–orbit interaction is caused by the mutual action of n-and π-electrons in molecules in the fluorescence state. Compounds of the quinoline family are important probes for the sensing of halides as well as have medicinal importance. Moreover, they have been projected as potential cation sensors particularly for Zn sensing in the recent years.

It has also been noticed that in case of 8-methylquinolinium (8-MQ), the L_{a} absorption shifts to the red and appears as a shoulder in the spectrum. This particular behaviour for 8-MQ has been explained on the basis of hyper-conjugation effect. Quinoline has been found to exhibit only phosphorescence in nonpolar medium but fluorescence is observed in hydrogen bonding solvents as well as on protonation. In non-polar medium, the lowest excited state is an n–π* state from which efficient inter-system crossing can occur. However, the main deactivation pathway in quinoline is intersystem crossing which is decreased in case of proton accepting medium as the n–π* state is raised and emission occurs from the π–π* state. However, the same compounds also show fluorescence in hydroxylic solvents such as alcohols, in which a hydrogen bond can be established between the nitrogen atom of the molecule and the hydrogen atom of the OH group of the alcohol molecule on the other. In such cases the
quantum yield of fluorescence and phosphorescence considerably depends on both the solvent and the temperature. Also, charged cations of these compounds derived from the acidified aqueous solution (1N H$_2$SO$_4$) have been used as standards for quantum yield because of high photostability and good fluorescence quantum yield. The present thesis has been organized into six chapters as follows:

**Chapter 1: GENERAL INTRODUCTION.**

The literature review, origin of the problem and its importance is referred here. In this chapter, history and the basic information about quinoline ring and their derivatives are provided. Since, quinoline and its derivatives are used in variety of the field (such as pharmaceutical, industrial, sensor, organic light emitting diodes etc.), therefore a brief discussion about their uses is presented. Chapter also provides the fundamental knowledge of spectroscopic terms and few important definitions, which are necessary to be understood for rest of the discussions.

**Chapter 2: METHODOLOGY: EXPERIMENTAL TECHNIQUES AND COMPUTATIONAL SIMULATION**

This chapter explains briefly about various experimental and computational techniques which are used throughout the study and to produce our results. Instrumentations of absorption spectroscopy, fluorescence spectroscopy in steady state and time domain and thermal coating unit is discussed here. For all the electronic structure calculation including ground state and excited state (linear response and state specific), DFT and TD-DFT calculations have been performed. Vibronically resolved spectra were obtained using overlap integral calculation of vibrational wave functions of ground state and first excited state.

**Chapter 3: ELECTRONIC AND VIBRONIC STRUCTURAL STUDIES AND PHOTO-PHYSICS OF PROTONATION OF QUINOLINE.**

Within this chapter, the study of spectral and photo-physical properties of quinoline and its protonated species is presented. Quinoline shows vibronic details in absorption
Abstract

spectrum and corresponding large Stoke shifted broad fluorescence emission spectrum having very low quantum yield and dual fit in decay time, however protonated quinoline shows red shifted fluorescence spectrum with increase in quantum yield and fluorescence decay tends to fit mono-exponentially. We present here, the systematic study of quinoline and protonated quinoline to understand the vibronic structure of absorption spectra and photo-physics of protonation of quinoline, both vibronic and electronic structure studies of quinoline (Q) and protonated quinoline (QH+) were carried out using GAUSSIAN 09. Normal mode mixing is taken into account by the Duschinsky transformation. The vibronic structure of strongly dipole-allowed transitions is calculated within the Franck–Condon approximation. A good correlation between theory and experiment is found to understand the photo-physics of protonation of quinoline. We revisited the experimental exploration of photo-physics of quinoline and its protonated form and found that the absorption spectrum of protonated quinoline is actually structured and IR activity of these fundamental units in ground state, Franck-Condon state and relaxed state is presented.

**Chapter 4: EFFECT OF ELECTRIC FIELD ON PHOTO-PHYSICS OF QUINOLINE.**

The chapter is based on pure computational work. The electroabsorption (E-A) and electroemission (E-F/E-Pl) or literally Stark spectroscopy of quinoline is discussed on the basis of GAUSSIAN calculations. Stark spectroscopy is a very powerful tool to obtain some change in molecular parameters and to understand some more aspects. The E-A and E-Pl spectra of quinoline were found to have the negative first derivative shape of absorption profile leading to the fact that the whole spectral change is governed by polarizability. The negative first derivative profile shape confirms that the change in polarizability is negative. The change in dipole moment from ground state to excited state was found to be nearly -0.50 D, while change in polarizability was estimated to be nearly -51 Bohr$^3$. The amplitude of E-A and E-Pl increases with the increase in the strength of the field. It was also found that quinoline shows circular dichroic activity when field is applied normal to the plane of molecule. Both the absorption and emission spectra show positive Cotton effect and this activity increases with increase in field. The variation of dipole moment vector with the field in ground state and excited state is
Abstract

reported which is found to be linear. The variation of dipole moment vector in excited state is steeper than in ground state. We also present the angle dependence of field on the dipole moment and polarizability components.

Chapter 5: NEAR FIELD EFFECT OF SILVER NANOPARTICLES ON THE PHOTOPHYSICS OF QUININE SULPHATE AND ITS DI-CATION DOPED IN POLYVINYL ALCOHOL THIN FILM

This chapter discusses the photo-physics of quinine sulphate (QS) and its dication (QSD) doped poly vinyl alcoholic film close-to silver nanoparticles. The enhancement in the absorption and emission spectra were observed due to coupling of surface plasmons with field of radiation. The absorption of quinine sulphate shows nearly 4 fold enhancement in absorption spectrum while fluorescence enhancement was found to be ~5000 fold. This huge enhancement in fluorescence is field effect of metallic nanoparticle literally known as metal enhanced fluorescence (MEF). Comparatively less enhancement in absorption (~2 fold) and fluorescence (~7 fold) was observed in case of quinine sulphate dication. This little enhancement in fluorescence is attributed to the chemical enhancement due to the bonding between metallic nanoparticles and fluorephores. The emission spectrum of QS on excitation at red Edge of absorption band shows a continuous shift towards lower energy side (EERS effect). The excitation dependence of the emission of polar aromatic molecules in viscous polar solvents is a common feature and is related to micro environmental heterogeneity. The QSD shows relatively less magnitude of EERS as compared to QS.

Chapter 6: PHOTOPHYSICS OF 5-AMINOQUINOLINE IN ACETONITRILE: WATER BINARY SOLVENT MIXTURE: REVISITED

Photo-physics of 5-aminoquinoline (5AQ) in acetonitrile-water binary mixture has been studied in this chapter. Fluorescence characteristics of 5AQ have been found sensitive to polarity of the medium (environment) as well as hydrogen bond donor capability. It is found that peak corresponding to $\pi$– $\pi^*$ shifts towards higher energy side and fluorescence shifts towards lower energy side. The experimental and computational observations suggest that this shift in spectral maxima in absorption and emission spectra was found as the consequence of the effect of H-bonding. It was reported that the stokes shift increases dramatically when
Abstract

amount of water is increased in the solvent but our study reveals that stokes shift does not increase since water makes complexes with the 5AQ in ground state.

List of Publications:

Published:


Communicated:


Abstract
