Density Functional Study of Low-Lying Electronic Excitations in Dipolar Ruthenium(II) Complexes

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Introduction

The design of new molecular materials with large second-order nonlinear optical properties (NLO) is currently the subject of extensive investigations by theoretical and experimental methods, since they have been expected to be used as frequency doubler, electrooptic modulator, and photorefractive media [1]. Within this field, an increasing amount of attention has recently been paid to organotransition metal complexes which offer possibilities for combination of NLO effects with many superior characteristics, such as ultrafast response times, lower dielectric constants, better processability as thin-film devices, and enhanced non-resonant NLO responses.

Usually, chromophores possessing large molecular hyperpolarizability contain donor (D) and acceptor (A) groups linked through a π − backbone. The NLO properties of such polarizable dipolar compounds are caused by intense, low energy $D(\pi) \rightarrow A(\pi^*)$ charge-transfer (CT) transitions [1].

A number of ruthenium (II) NLO active complexes were studied in details using hyper-Rayleigh scattering and Stark spectroscopy techniques [2-6]. There were established that NLO properties of these compounds are caused by strong metal-to-ligand charge transfer (MLCT) and the strong solvatochromic effect have been demonstrated [6]. The most recent experimental and theoretical study of the effects of polyene chain extension on the NLO properties of ruthenium (II) pyridil complexes was done [3]. Density functional theory (DFT) based on B3P86 hybrid functional [7] without solvent effect consideration gave rise to only qualitative description of experimentally observed trends. Moreover, these calculations predict that the change of dipole moment ($\Delta\mu$) caused by the low-energy MLCT decreases with the polyene bridge length growth. In the present paper we will study ruthenium (II) ammine complexes in solution to develop accurate and reliable theoretical description of NLO properties of organometallic and coordination compounds.

In the present contribution, we examine B3P86 DFT functional to investigate excited state properties E, μ and $\Delta\mu$ of ruthenium (II) ammine complexes (see Fig. 1) to establish the influence of solvent on electronic properties of organometallic chromophores in details. Obtained theoretical results demonstrate a good agreement with experimental data

and proposed approach can be useful tool for design of new NLO active organometallic and coordination compounds.
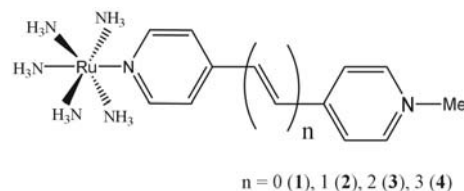

Figure 1: Chemical structures of cations investigated.

Computational Details

All theoretical calculations were performed by the Gaussian 03 [8] program. B3P86 functional and LANL2DZ basis set were used and the molecular geometries were optimized assuming *Cs* symmetry. For each molecule two different optimized structures were obtained. Namely, all molecules were optimized using B3P86 and Hartree-Fock (HF) approaches. Electronic transitions were calculated by means of time-dependent DFT (TDDFT) method [9]. Differences of dipole moments between ground and *n*-th excited states were estimated using both of finite-field (± 0.001 a.u.) [10] and RhoCI calculation methods. Experimental studies of investigated systems were carried out in acetonitrile (MeCN) at room temperature and butyronitrile (PrCN) glasses at 77 K [3, 4]. Since at present time modeling in butyronitrile solution is unavalable in Gaussian 03 program, we restrict ourself by study systems in MeCN only. Solvent effect on the excited states were examined using Onsager polarizable point dipole moment models [11].

Results and Discussion

A numerical data for cations **1 – 4** calculated by B3P86 method for different geometries in MeCN solution comparing with experimental results are plotted in Fig. 2. Our calculations in gas phase for DFT optimized structures give same results for the values of E and μ like published in [4]. Finite field and RhoCI calculations results of $\Delta\mu$ in the gas phase are different but both of these approaches give very poor numerical agreement with experiment.

To compare the theoretical and experimental results correctly it is necessary to denote that MLCT

bands of investigated chromophores undergo marked red-shifts with temperature decreasing [5]. The measured changes in E on moving from 298 to 77 K are -0.15 and -0.23 eV for complexes **1** and **2** in PrCN solution, correspondingly. At the same time, the values of oscillator strength f_{os} that are directly related to transition dipole moment μ show very little temperature dependence ($\leq 5\backslash\%$) [2].
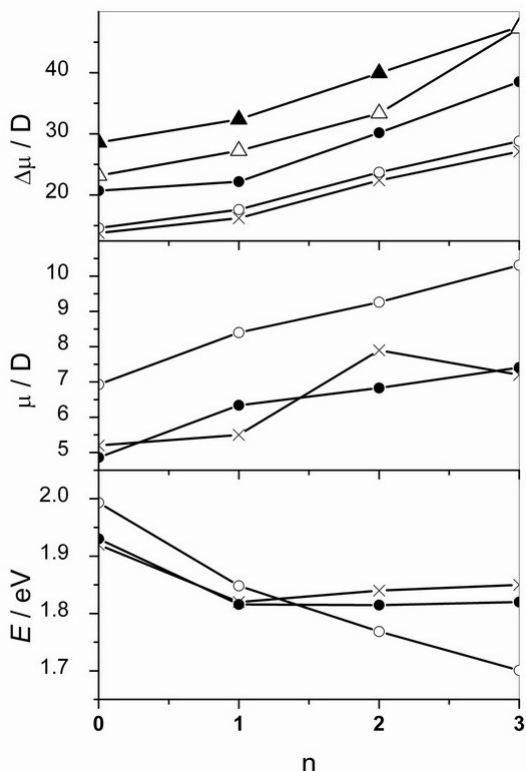

Figure 2: Values of $\Delta\mu$, μ and E: experimental (x) and calculated using B3P86 (open symbols) and HF (solid symbols) optimized structures. For $\Delta\mu$ values results for both of finite-field and RhoCI calculation results are plotted (triangles).

For DFT optimized structures the values of E and $\Delta\mu$ have been calculated with good accuracy and an error for values μ have been found. Using HF optimized structures, E and μ values are obtained in a good agreement with experiment but $\Delta\mu$ are strongly overestimated. It is seen that for values of μ and $\Delta\mu$ calculated DFT and HF optimized structures demonstrate similar functional behavior. But there is numerical agreement with experiment for μ and disagreement for $\Delta\mu$ when DFT optimized structures were used and vise versa for HF optimized structures. Calculated E is steadily decreasing function of n for DFT structures but for HF ones $E(n)$ demonstrate better agreement with experiment. We also performed RhoCI calculations of $\Delta\mu$ values in MeCN solution to compare the accuracy of different calculation methods. The RhoCI calculated values of $\Delta\mu$ demonstrate same tendency of change like experimental one but are approximately two times overestimated (Fig. 2).

Considering also that in two-state model [12] the first static hyperpolarizability is squared function of (μ/E) and linear one of $\Delta\mu$ we can conclude that for calculation of this value using the HF optimized structures have to give better numerical results.

Besides the reducing of the absorption energy there is also effect of solvent on the electronic properties of investigated complexes. Gas phase calculations predict that the change of dipole moment $\Delta\mu$ decreases with the polyene chain length growth. However, the study of these compounds in solution gives a steadily increasing of this value that is in a good agreement with experiment [3]. Analysis of molecular orbitals demonstrates that in the case of long molecules **3** and **4**, the solvent effect is not restricted only by absorption energy change but MLCT becomes more intensive too. Another one difference between gas phase and MeCN solution for compounds 3 and 4 is that the MLCT is caused by (HOMO-3, HOMO) $\rightarrow$ LUMO transition in the gas phase and HOMO $\rightarrow$ LUMO in solution.

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