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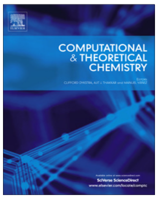

DFT study of potential energy surfaces and conical intersection structures of Rhenium(I) tricarbonyl diimine complexes

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Potential energy surfaces of the ground and lowest excited states of $[Re(CO)_3(phen)L]^q$ (L = imH, $q = +1$; L = Cl, $q = 0$) complexes were investigated by TDDFT methods in gas phase and solvent. Two (in gas phase) or three (in solvent) tautomeric structures, differing by the angle of rotation of the imidazole ligand around the Re–N bond were found for $[Re(CO)_3(imH)(phen)]^+$. Excited state minima of the lowest singlet and triplet states were found, and luminescence energies were calculated. 11 conical intersection (CI) structures in total were obtained. Three common types of CI's were found both for $[Re(CO)_3(imH)(phen)]^+$ and $[Re(CO)_3(Cl)(phen)]$, and additional CI type was found only for $[Re(CO)_3(imH)(phen)]^+$. Every CI type of $[Re(CO)_3(imH)(phen)]^+$ corresponds to two CI structures, differing by the angle of rotation of the imH ligand.

1. Introduction

Rhenium(I) tricarbonyl diimine complexes $[Re(CO)_3(N,N)L]^q$ exhibit exceptionally rich photophysical properties that can be easily tuned by variation of ligand structures or medium [1–3]. Combined with chemical flexibility and stability, these properties make these complexes notably attractive photosensitizers and probes. These complexes have a wide range of application, including biomolecule labeling [4–8], photocatalytic CO_2 reduction [9,10], molecular switches [11–14], sensors [15,16] and light emitting devices [17].

For a detailed theoretical understanding of the photophysical processes, it is important to build at least a general structure of the potential energy surfaces (PES) of the ground and first excited states. Until recently, quantum chemical studies of the PES of excited states were limited to the discussion of their possible forms and correlation diagrams connecting reagents and products. For a certain period, the discussion was focused on the problem of how the system in the excited state reaches the ground state [18–20]. Much earlier, in 1937, Teller [21] showed that for polyatomic molecules, the intersection of the potential surfaces of the states of the same symmetry (and multiplicity) can be described in terms of the so called conical intersections (CI). The conical intersections are named after the form of the PES in the vicinity of the crossing points in the space of two specially chosen coordinates. Such intersections are regarded as the "funnels", through which the transitions mentioned above occur with very high speed [22,23]. The general theory of the properties of the conical intersection was later developed by Yarkony and Baer [22,24]. The final recognition of this theory was based on the progress in modern computational quantum chemistry. The methods of search of conical intersections include the use of the CASSCF approximation [25]; later, the approach based on Density Functional Theory was developed [26]. The study of organic compound reactions showed that the mechanisms based on transitions through CI are not rare events. More details can be found in [27–30]. As for the transition metal complexes, only a few studies in this field of chemistry are known [31–37]. As a rule, the prediction of the CI positions is a difficult problem. In the case of organic compounds, the search for CI is facilitated by the valence theory approach. The situation is quite different for transition metal compounds: in fact, there are no definite hybrid orbitals for the metal atoms.

In organic compounds, there is usually only one CI of the **S0/S1** type. However, in general, the number of such intersections remains unclear. According to Truhlar [38], the existence of the minimum of the energy gap between the PES of the neighboring states is an indication of the high possibility of finding a CI in the nearest points of configuration space. Conical intersections are not rare; true avoided crossings are much less likely.

The goals of this work are to determine the frequent emergence of CIs between the electronic states PES's of transition metal complexes; to describe the corresponding states in terms of the standard classification of the electronic transitions in the compounds

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under study; to find the common features of the CIs in the complexes that have a common structure of metal-ligands bonds. As the objects of investigation, we chose two rhenium tricarbonyl complexes, $[Re(CO)_3(imH)(phen)]^+$ and $[Re(CO)_3(Cl)(phen)]$. These complexes were recently studied both experimentally and theoretically [39,40].

In the heavy transition metal compounds the additional feature that has to be taken into account is spin-orbital coupling (SOC). This problem was discussed in review article [40] using the Rhenium(I) complex $[Re(CO)_3(imH)(phen)]^+$ as an example. It was mentioned that SOC in the complexes with wide electronic delocalization over accepting ligands is strongly reduced as compared with the free transition metal atoms. Our test calculations for the compounds under consideration showed that there is no noticeable SOC between the lowest spin singlet and triplet states in the vicinity of the points of conical intersections. So in this work we use spin-free approach in the search of the conical intersections. We are going to return to the effect of SOC later.

2. Calculation details

All calculations were performed by the DFT/TD-DFT method with the hybrid exchange-correlation functional PBE0 [41,42]. The Lanl2DZ basis set with relativistic effective core potentials [43] was used for the Re atom, and the 6-31G basis set was used for the C, O, N and H atoms. At the special points (ground and excited state minima and CIs) the calculations were repeated using the 6-31G(d) basis set and B3LYP functional (see Tables 1–4 in supplementary materials). All the calculations except the search for conical intersections were performed using Gaussian 09 software [44], both for isolated and solvated complexes, using the PCM [45] model for DMF. Conical intersection points were obtained by GAMESS-US software [46] for isolated complexes using the Tamm–Dancoff approximation [47]. All calculations were performed using computational resources provided by the Resource Center "Computer Center of SPbU".

To investigate the potential energy curves between two structures, Z-matrices were fixed for these structures and all geometry parameters were linearly interpolated. The resulting potential curve is dependent on the chosen set of independent parameters (Z-matrix), and the minimum energy path lies lower or equal to the obtained path. Therefore, the existence of a potential barrier on the calculated curve could result from an imperfect choice of Z-matrix, but the absence of a potential barrier on the calculated curve indicates that on the minimum path a barrier is also absent. To build a real transition path, one must calculate the complete multi-dimensional structure of PES, which is impossible at present.

Electronic spectra were calculated at all intermediate points. Spectra in adjacent points were correlated with each other to build a curve for each electronic state.

3. Results and discussion

Here and below we will use lowercase letters to denote electronic states: **s0** stands for the ground state, **s1** – for the first excited singlet state and **t1** – for the first excited triplet state. For the corresponding minima structures, we will use capital letters: **S0** is the ground state minimum, or the equilibrium structure, **S1** and **T1** are the minima of the corresponding states.

3.1. Equilibrium structures

For $[Re(CO)_3(imH)(phen)]^+$, two equilibrium structures, **S0/A** and **S0/B**, were found in the absence of solvent and three, **S0/A**, **S0/B**, and **S0/C**, – in the presence of solvent (see Fig. 1). All the equilibrium structures differ mainly by the angle of rotation of the imidazole ligand around the Re–N bond. Structures **S0/A** and **S0/B** have Cs symmetry, structure **C** – C1 symmetry. In the gas phase, the **S0/B** state is lower in energy than the **S0/A** state, and in solution **S0/C** has the lowest energy. However, the energy difference between all structures is very small, and as seen in Fig. 2, the potential barrier of rotation is also low, approximately 1.5 kcal/mol in the absence of solvent and 1 kcal/mol in the presence of solvent. Thus, the structures found can be considered as tautomeric species. Experimental structure for solid sulfate [48] is rather close to structure **C**.

For $[Re(CO)_3(Cl)(phen)]$, one equilibrium structure was found. The local symmetry at the metal center differs from that of the ideal octahedron by a small tilt of the $Re(CO)_3Cl$ group, so that the Cl atom is slightly closer to the phen ligand than the axial CO group. This structure is in good agreement with the experimental structure [49] (see Fig. 3).

For both complexes, solvation has very small influence on the equilibrium structures, except for the presence of the new **S0/C** structure for $[Re(CO)_3(imH)(phen)]^+$. (See attached mol files).

3.2. Excited states

Characters of the low-lying states at equilibrium geometries are given in Tables 1 and 2. All states have strongly mixed character. Lowest singlet states correspond to $[Re(CO)_3] \rightarrow L$ transition (imH complex) or $[Re(CO)_3Cl] \rightarrow L$ transition (Cl complex), and most triplet states include additional intraligand ($L \rightarrow L$) component. Characters of $[Re(CO)_3(imH)(phen)]^+$ states and $[Re(CO)_3(Cl)(phen)]$ singlet state differ slightly in gas phase and solution, while $[Re(CO)_3(Cl)(phen)]$ triplet states exhibit unexpectedly large character change, so that in absence of solvent they have no IL component. In all cases solvation leads to increase in excitation energies, which seems to be larger for pure charge transfer singlets of both complexes than mixed IL/CT triplet excitations of imH complex. This might indicate weaker solvation of CT excited states.

Lowest excited states were calculated at every structure mentioned in this article using B3LYP and PBE0 functionals and 6-31G and 6-31G(d) basis sets for all non-Rhenium atoms. Results are listed in Tables 1–4 of supplementary materials. In general, B3LYP calculations provide lower excited state energies, than PBE0, while basis set change leads to change of relative energies of ground states at different geometries.

3.3. Excited states minima

For the **s1** state in the absence of solvent, two minima structures were found for $[Re(CO)_3(imH)(phen)]^+$ and one for $[Re(CO)_3(Cl)(phen)]$. All structures are very close to the corresponding equilibrium states: **S0/A** and **S0/B** for $[Re(CO)_3(imH)(phen)]^+$ and **S0** for $[Re(CO)_3(Cl)(phen)]$. All **S1** structures differ from the corresponding **S0** states by small changes of valence angles. For $[Re(CO)_3(imH)(phen)]^+$, **S1** differs by a small increase of the C2–Re1–C3 angle and a decrease of the C1–Re1–N1 angle so that all four monodentate ligands become closer to the phen ligand, and for $[Re(CO)_3(Cl)(phen)]$, **S1** is characterized by a more regular octahedral structure than **S0**.

For the **t1** state in the absence of solvent, two minima structures were also found for $[Re(CO)_3(imH)(phen)]^+$ and one for $[Re(CO)_3(Cl)(phen)]$. Similarly to **S1**, the **T1** structures are located close to the corresponding **S0** structure and differ by angle changes in the rhenium surroundings. Both **T1** states are asymmetric: for $[Re(CO)_3(imH)(phen)]^+$, the **T1** state is characterized by rotation of the imH ligand around the Re–N bond by 15–20°, and for $[Re(CO)_3(Cl)(phen)]$, the **T1** state differs by small rotation of the $Re(CO)_3Cl$ group around the line connecting the Re atom and the center of the phen ligand.