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Applicability of density functional and wave function theories combined with the three-dimensional reference interaction site model self-consistent field method to the d–d transitions of a transition metal aqua complex

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Abstract. The applicability of density functional theory (DFT) and wave function theory combined with the three-dimensional reference interaction site model self-consistent field method to the d–d transitions of transition metal aqua complexes was examined using $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in aqueous solution as an example. DFTs with hybrid functionals, multiconfigurational self-consistent field followed by perturbation theory, and coupled-cluster singles and doubles (CCSD) followed by the equation of motion CCSD, gave reasonable d–d transition energies.

1. Introduction

Transition metal compounds are widely known to exhibit a variety of colors. Therefore, transition metal salts and oxides have been used as colorants in glass and ceramics, and as pigments in paintings. Transition metal complexes in solution also exhibit a variety of colors. These properties are due to the fact that the central element of the metal complex is a transition element, and the d or f orbitals are not completely filled with electrons.

The d–d transition is an electronic transition between the split d orbitals. The d–d transition energy is in the range of 1–4 eV. This corresponds to the wavelength range of 300–1200 nm, which covers the visible light wavelength range of 360–800 nm. To elucidate the optical properties of transition metal complexes, a number of experimental and theoretical studies have been conducted.

Previously, we reported on the molecular and solvation structures and excitation spectra of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cu}(\text{H}_2\text{O})_4-6]^{2+}$ in aqueous solution using the three-dimensional reference interaction site model self-consistent field (3D-RISM-SCF) method.[1,2] These two systems are of a rather different nature in terms of electronic structure. Since $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is a d_3 system, the ground state is nondegenerate and the octahedral complex is stable. On the other hand, $[\text{Cu}(\text{H}_2\text{O})_4-6]^{2+}$ are d_9 systems, and therefore the ground state is quasidegenerate in octahedral symmetry, resulting in distorted geometries due to the Jahn–Teller effect. In both cases, density functional theory (DFT) with global hybrid generalized gradient approximation (the B3LYP and PBE0 functionals) worked well. However, the applicability of other exchange–correlation functionals and wave function theory (WFT) has not been clarified. In the present study, we examine their applicability to the d–d transitions using the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ system as an example.



2. Method

2.1. 3D-RISM-SCF method

The 3D-RISM-SCF method is a hybrid method of the electronic structure theory and integral equation theory of liquids (3D-RISM theory).[3,4] In this method, solute molecules are treated quantum-chemically and solvent molecules are treated statistical-mechanically; thereby, the electronic wave function of the solute and the distribution of the solvent (spatial distribution function (SDF), $g_s(\mathbf{r})$; s indicates the solvent site) around the solute are determined simultaneously.

The Helmholtz energy of a system (A) is defined as the sum of the solute electronic energy (E_{solute}) and the excess chemical potential ($\Delta\mu$)

$$A = E_{\text{solute}} + \Delta\mu \quad (1)$$

E_{solute} is calculated from electronic structure (density functional or wave function) calculation; hence, it is a functional of an electron density $E_{\text{solute}}[n]$ or a wave function $E_{\text{solute}}[\Psi]$. $\Delta\mu$ is calculated from the equation

$$\Delta\mu = \rho k_B T \sum_s^{\text{solvent-sites}} \int d\mathbf{r} \left[\frac{1}{2} (h_s(\mathbf{r}))^2 \theta(-h_s(\mathbf{r})) - c_s(\mathbf{r}) - \frac{1}{2} h_s(\mathbf{r}) c_s(\mathbf{r}) \right] \quad (2)$$

where k_B and T indicate the Boltzmann constant and the absolute temperature, respectively, and ρ is the number density of the solvent. The functions $h_s(\mathbf{r}) = g_s(\mathbf{r}) - 1$ and $c_s(\mathbf{r})$ are the 3D total and direct correlation functions of solvent site s , respectively, and $\theta(x)$ is the Heaviside step function. The Kovalenko–Hirata (KH) closure[3,5] is used to derive equation (2). 3D correlation functions can be obtained by solving the 3D-RISM equation

$$h_s(\mathbf{r}) = c_t(\mathbf{r}) * (\omega_{ts}^{\text{vv}}(r) + \rho h_{ts}^{\text{vv}}(r)) \quad (3)$$

coupled with the KH closure, where $\omega_{st}^{\text{vv}}(r)$ and $h_{st}^{\text{vv}}(r)$ are the site–site intramolecular and total correlation functions of the solvent, respectively (superscript v denotes the solvent). The symbol $*$ indicates convolution in direct space and summation over repeated site indices. Before carrying out the 3D-RISM calculation, we need to solve the (1D) RISM equation between the solvent molecules

$$h_{st}^{\text{vv}}(r) = \omega_{ss'}^{\text{vv}}(r) * c_{s't'}^{\text{vv}}(r) * (\omega_{t't}^{\text{vv}}(r) + \rho h_{t't}^{\text{vv}}(r)) \quad (4)$$

and obtain $h_{st}^{\text{vv}}(r)$ in equation (3), where $c_{st}^{\text{vv}}(r)$ indicates the site–site direct correlation function of the solvent molecules.

2.2. Computational details

We performed the 3D-RISM-SCF calculations for the ground state in aqueous solution and excited state calculations for the d–d transitions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ using the solvation structure of the 3D-RISM-SCF method. The molecular structure of the ion was optimized using the solvation model based on density (SMD), proposed by Marenich et al.[6] The basis sets used were the 6-311G(d,p) basis set[7] for H and O, and the Wachters–Hay all-electron basis set [8,9] supplemented with one f-function (exponent: 0.87) for Cr. The electronic structure theories used in the 3D-RISM-SCF method were DFT with several exchange–correlation functionals [BLYP, PBE, and OLYP (pure generalized gradient approximation (GGA)); B3LYP, PBE0, and X3LYP (global hybrid (GH) GGA); TPSS and revTPSS (pure meta-GGA (mGGA)); TPSSh (GH-mGGA); and CAM-B3LYP (range-separated hybrid (RSH) GGA)], [10] and also the Hartree–Fock (HF), complete active space self-consistent field (CASSCF), [11] and coupled-cluster singles and doubles (CCSD)[12] methods. For excited state calculations, the time-dependent (TD) HF, TDDFT, state-averaged (SA) CASSCF, multiconfigurational quasidegenerate perturbation theory (MC-QDPT), [13] and equation of motion (EOM) CCSD[12,14,15] were also used. In the CASSCF method, the active space was constructed by distributing three electrons in 10 orbitals (3d- and 4d-like orbitals). The parameters in the 3D-RISM calculations were the same as reported previously.[1]

Table 1. First and second d–d transition energies of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in aqueous solution (eV).

Method ^a	Optimized geometry			PBE0 geometry	
	$4T_{1g}$	$4T_{2g}$	$d(\text{Cr-O}) / \text{Å}$	$4T_{1g}$	$4T_{2g}$
HF/TDHF	1.53	3.08	2.080	1.78	3.32
DFT/TDDFT					
BLYP	2.06	2.48	2.045	2.06	2.48
PBE	2.13	2.49	2.026	2.16	2.53
OLYP	1.86	2.17	2.057	2.06	2.38
B3LYP	2.10	2.73	2.036	2.09	2.73
PBE0	2.15	2.80	2.020	(2.15)	(2.80)
X3LYP	2.09	2.76	2.034	2.16	2.82
TPSS	2.39	2.87	2.022	m	2.88
revTPSS	2.46	2.96	2.018	2.46	2.96
TPSSh	2.39	2.98	2.020	2.40	2.98
CAM-B3LYP	2.29	2.85	2.020	2.18	2.85
CASSCF/SA-CASSCF	1.81	2.85	2.000	1.72	2.74
CASSCF/MC-QDPT	1.97	2.87	2.000	1.88	2.90
CCSD/EOM-CCSD	1.81	2.97	2.048	1.95	3.12
Exp. ^b	2.11	2.98	1.96–2.03 ^c		

^a The notation A/B indicates that the 3D-RISM-SCF and excitation energy calculations were performed using the A and B methods, respectively. ^b Reference 16. ^c Reference 17.

3. Results and discussion

Table 1 shows the transition energies of two d–d transitions ($4T_{1g}(\text{F}) \leftarrow 4A_{2g}(\text{F})$ and $4T_{2g}(\text{F}) \leftarrow 4A_{2g}(\text{F})$). In the table, the Cr–O distances are also listed. All the geometries optimized were in T_h symmetry; hence the six Cr–O distances are all equal.

The method not including electron correlation, i.e., the HF method, gives a rather long Cr–O bond distance of 2.080 Å, compared with the experimental value range of 1.96–2.03 Å. The transition energies by HF/TDHF at the optimized geometry are 1.53 and 3.08 eV. The deviation of the lower transition energy from the experimental value is not small (–0.58 eV). The DFTs with various exchange–correlation functionals give somewhat longer Cr–O distances. The average distance is 2.03 Å, and four of 10 results are over the experimental value range of 1.96–2.03 Å. Many of the DFT/TDDFT give improved transition energies compared with the HF/TDHF. In particular, the results of the hybrid functionals (GH-GGA, GH-mGGA, and RSH-GGA) are in good agreement with experimental results. The average deviations from the experimental values are 0.11 and 0.16 eV for $4T_{1g}$ and $4T_{2g}$, respectively. In contrast, the deviations of pure functionals (pure GGA and mGGA) are 0.19 and 0.39 eV. The CASSCF Cr–O distance is 2.000 Å. The transition energies by CASSCF/SA-CASSCF are 1.81 and 2.85 eV, which are slightly underestimated. The CASSCF method takes account of only static electron correlation, not dynamic electron correlation. By also taking account of dynamic electron correlation, MC-QDPT (CASSCF/MC-QDPT) improves the transition energies, giving 1.97 and 2.87 eV. The Cr–O distance by CCSD is somewhat longer (2.048 Å) compared with that by CASSCF. The transition energies of CCSD/EOM-CCSD are 1.81 and 2.97 eV (the former is slightly underestimated).

Table 1 also shows the transition energies at the PBE0 optimized geometry; the trend of each theoretical method can be seen by excluding the geometry effect. The results show that the DFTs tend to underestimate the $4T_{2g}$ energy (average 2.74 eV), while the wave function theories (CASSCF, MC-QDPT, and EOM-CCSD) tend to underestimate the $4T_{1g}$ energy (average 1.85 eV).

Figure 1 shows the radial distribution functions (RDFs) of O and H atoms around the Cr atom, which are obtained by angular averaging of the SDFs by 3D-RISM-SCF. Each method gives very similar RDFs. The peak positions are 4.0 and 4.9 Å, corresponding to the experimental values of 4.0 and 4.5 Å,[17]

respectively. These peaks indicate the second hydration shell around the Cr^{3+} ion, which is mainly composed of solvent water molecules that form hydrogen bonds with the ligand water molecules.

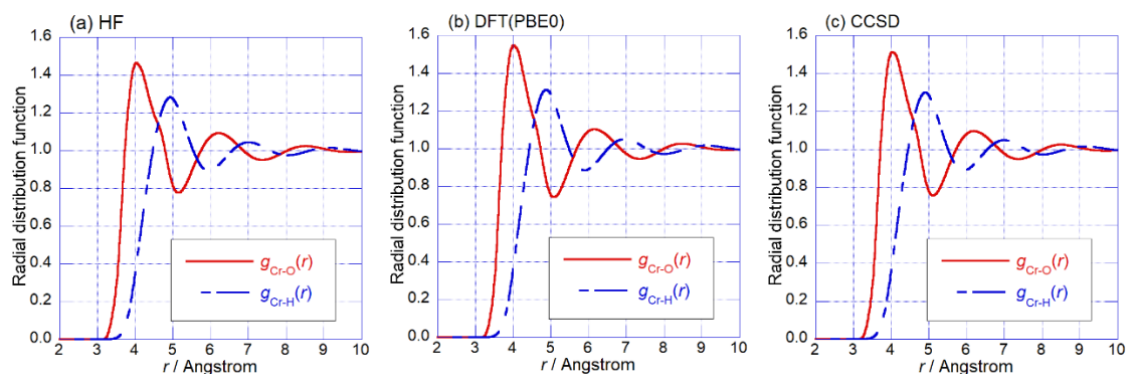


Figure 1. Radial distribution functions calculated by angular averaging of spatial distribution functions of the 3D-RISM-SCF with (a) HF, (b) DFT(PBE0), and (c) CCSD.

4. Summary

We have examined the geometry, d–d transitions, and solvent distribution functions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in aqueous solution, which is an example of a transition metal complex with a nondegenerate ground state. The DFTs with hybrid functionals work well for the d–d transitions. The wave function theories also give reasonable results. The distribution functions of solvent obtained by 3D-RISM-SCF are similar, which are almost independent of the electronic structure methods.

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