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Research paper

Excitation spectra of Ag_3–DNA bases complexes: A benchmark study

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ABSTRACT

Assessment of different *ab initio* and TDDFT methods was studied for calculation of the excitation energies of the complexes of pyrimidine bases with positively charged Ag_3^+ clusters. Performance of CIS, CIS(D), CC2, ADC(2), MP2, and TDDFT techniques with the use of different hybrid–GGA and meta–hybrid–GGA functionals and basis sets is studied. We found that M06–2X functional shows good accuracy in comparison with the ADC(2) *ab initio* method and that the geometry optimization approach can strongly affect the excitation spectra of the complexes. Our results may have important implications for further studies of ligand–stabilized silver nanoclusters.

1. Introduction

DNA–based fluorescent Ag clusters have attracted a lot of attention in the past years due to their potential applications in material science and nanophotonics [1–3]. Few–atom silver nanoclusters stabilized by DNA have much greater brightness, photostability and biocompatibility compared to organic fluorophores [4,5], which makes them nearly ideal fluorophores for biological labeling [6–11]. However, detailed structures of the fluorescent Ag_nDNA complexes remain unknown due to the high heterogeneity and the absence of crystal structure data for such systems. Theoretical calculations using quantum chemistry techniques appear as one of the most promising tools for determining the structure and electronic proper-ties of Ag_nDNA systems.

In our recent paper [12], we have suggested a combined experimental and theoretical approach for determining the structures of such complexes. That approach is based on the simulation of fluorescence excitation spectra of Ag_nDNA complexes. However, it requires robust QM/MM calculations. It should be noted that only a few studies have dealt with QM calculations of excitation spectra of metal-ligand complexes [12–21]. Only two of them are relevant to the fluorescence species [12,18]. All of them, except for the work [12] have used the time–dependent density functional theory (TDDFT) approach. Meanwhile, the studies on Ag_nDNA systems showed a presence of charge–transfer (CT) transitions [15,18]. It is well–known that TDDFT methods significantly underestimate energies of charge–transfer (CT) states, which makes such approaches inappropriate for accurate modeling of the absorption spectra. On the other hand, even propagator–based approaches, especially second–order algebraic diagrammatic construction scheme (ADC(2) [22]) that have recently gained a lot of attention as a promising compromise to more computationally expensive methods, are limited to medium–size systems and cannot describe behavior of real Ag_nDNA complexes as well.

To the best of our knowledge, there are no benchmark studies for the excited states calculations of small Ag clusters interacting with nucleobases. That is why finding a cost–effective strategy for real Ag_nDNA complexes is such an important and challenging task. In this work we focus our attention to a positively charged Ag_3^+ cluster stabilized by pyrimidine bases since Ag_3^+ clusters have been identified as emitting centers in rare gas matrices [23,24], zeolites [25,26] and DNA [12]. We compare different computational approaches for the geometry optimization and excited states calculations of Ag_3^+–nucleobases systems. We also address a question on how the base-cluster bonding affects the excitation spectra of the clusters.

2. Computational details

In order to investigate the influence of different geometry optimization strategies on the excitation spectra of all complexes the gas phase molecular structures were optimized using second-order Møller–Plesset Perturbation theory with resolution of identity approximation (RI–MP2) [27] and at DFT/PBE0 [28–30] level

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of theory with use of def2–SVP basis set [31] for all calculations. No geometrical constraints have been applied. The calculations were performed using the Turbomole program package [32]. In our calculations, we refer to 1–methylcytosine as a cytosine monomer, and 1–methylthymine as a thymine monomer, since silver clusters bind to DNA bases and not to sugar–phosphate backbone [33,34]. Calculations of excited states of Ag_3^+ clusters and Ag_3^+–base complexes were made with different basis sets: def2-SVP, def2-TZVP [35] and aug-cc-pVDZ [36] (aug-cc-pVDZ-PP [37] for Ag atoms) basis sets for comparison. In all calculations we used def2-ecp [38] with 28 core electrons for Ag atoms. Test calculations showed that increasing of the basis set has a minor effects of ca 0.15 eV on the excitation energies (Tables 1 and 2 in SI). To reduce computational cost for calculations with more than two monomers, we used def2–SVP basis set for all the calculations reported in this study.

Excitation spectra were calculated using different approaches including wave–function techniques (CIS, CIS(D) [39], CC2 [40] and ADC(2)) and also TDDFT with 6 hybrid–GGA and meta–hybrid–GGA functionals with different amount of Hartree–Fock exchange (TPSSh [41] (10%), B3LYP [42] (20%), PBE0 [43] (25%), M06 [44] (27%), BHLYP [45] (50%) and M06-2X [44] (54%)). The RI [46] method, applied for CIS, CIS(D), CC2 and ADC(2), decreases the computational effort for the time–consuming two–electron integrals considerably. The advantage of the ADC(2) method is in use of a Hermitian secular matrix which is constructed by many–body perturbation theory. The ADC(2) was chosen as a reference method for comparison with the TDDFT results. All the DFT related calculations were performed with multiple m3 grid [47]. For TDDFT calculations we compared the Tamm–Dancoff approximation (TDA) and the random phase approximation (RPA) which is a parameter–free density functional with long–range dispersion interactions included. Comparison of excitation energies obtained with RPA and TDA approximations can be found in Table 3 in SI. Calculations with RPA approximation exhibit ca. 0.1–0.2 eV lower excitation energies compared to those obtained at TDA level of theory. However, it should be noted that the energies of CT states calculated within RPA and TDA approximations are practically the same and within 0.02 eV (Table 3 in SI). That is why we used RPA approximation in all TDDFT calculations. Functionals with less than 50 % of Hartree–Fock exchange put CT states on the first place for Ag_3^+–Thymine structures (Fig. 1 in SI). M06-2X functional with RPA approximation was chosen for the further comparison with ADC(2) method since it shows better performance over other functionals and calculated energies for Ag_3^+, Ag_3^+–Thymine and Ag_3^+–Cytosine lie within 0.1 eV compared to those calculated at ADC(2)/def2-SVP strategy. NTOs were obtained with TheoDore [48] program package and visualized with JMOL [49]. CT transitions were identified by visual analysis of obtained NTOs.

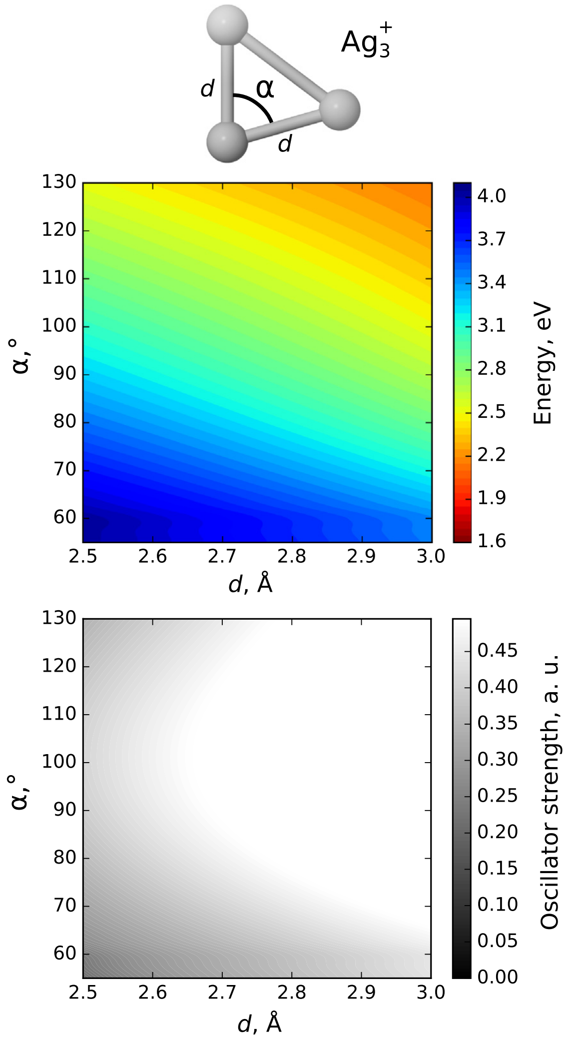
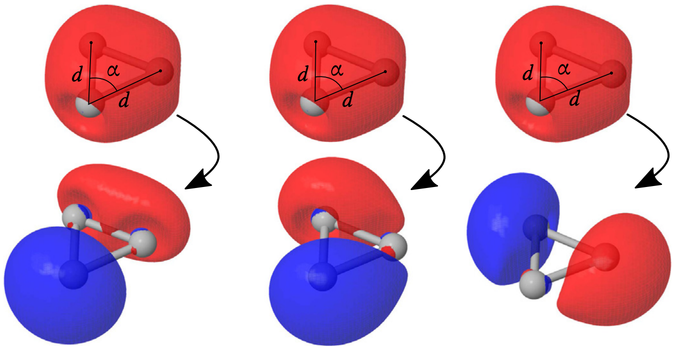


Fig. 1. Energies and oscillator strengths of the lowest transitions related to the different Ag_3^+ geometries calculated at ADC(2)/def2-SVP level of theory.



α = 58° α = 60° α = 62°

Fig. 2. Natural transition orbitals of the first transition for Ag_3^+ cluster with different angles α and $d = 2.7$ Å.

3. Results and discussion

In order to separate the effects of a cluster geometry change and alteration of the Ag–N/O bonds length on the excitation spectra of the complexes in comparison with isolated clusters we calculated excitation energies and oscillator strengths for the lowest transition of a free isosceles triangle Ag_3^+ cluster with side $2.5 \leqslant d \leqslant 3.0$ and angle $56^\circ \leqslant \alpha \leqslant 130^\circ$ at ADC(2)/def2-SVP level of theory. The obtained data are presented as a 2D plot in Fig. 1. Our results are in a good agreement with an earlier suggested idea that altering the bend angle of the Ag_3^+ cluster affects strongly its absorption spectrum [18]. The shape of the natural transitional orbitals (NTOs) (Fig. 2) depends only on the bend angle α and have different symmetry for different angles within $58^\circ < \alpha < 62^\circ$ it is also worth noting that all the structures with $\alpha \geqslant 62^\circ$ have similar NTOs even for different side size d.

In the next stage, we made ground state optimization for the Ag_3^+–(Thymine)$_n$ and Ag_3^+–(Cytosine)$_n$ complexes where $n = 1 - 4$ at MP2 and PBE0 levels of theory. Since resulted structures of complexes are very similar we pictured only those optimized at PBE0/