A Density Functional Analysis on the Photoelectronic Spectra of Fe-Only Hydrogenase Analogues

Eben Sy Dy and Hideaki Kasai
Department of Precision Science & Technology and Applied Physics,
Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Carl Redshaw and Christopher J Pickett
School of Chemical Sciences and Pharmacy, Faculty of Science,
University of East Anglia, Norwich, NR4 7TJ, U. K.
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Density functional theory calculations have been performed on Fe-only hydrogenase analogues compounds [(i-PDT)Fe₂(CO)₄(CN)]²⁻ (compound I) and [Fe₂(CO)₄MeSCH₂C(Me)-(CH₂S)₂(CN)]²⁻ (compound II). Results using BPW91/6-311+G(d,p) show electron affinity and trends in molecular orbitals consistent with photoelectron spectroscopy data. The HOMO orbitals show familiar Fe-Fe bonding characteristics while the LUMO orbitals show Fe-Fe anti-bonding characteristics. To compare the effects of a second CN versus a terminal sulfur ligand, results found that compound I after one electron is removed (compound I−1e) were compared with those of compound II. It was found that compound I−1e has a much lower HOMO. Mulliken charge analysis also shows that the terminal sulfur has a stronger electron donating effect than a CN ligand. From the standpoint of computational materials design, we therefore think that similarities in electron affinity, 2Fe charge density and HOMO/LUMO characteristics to the biologically present active site should be bases for predicting catalytic activity of Fe-only hydrogenase analogues. [DOI: 10.1380/ejssnt.2007.148]

Keywords: Density functional calculations; Photoelectron spectroscopy; Catalysis; Hydrogen Molecule; Hydrogenase; Hydrogen Oxidation and Evolution Reaction

I. INTRODUCTION

Fe-only hydrogenase is a class of enzyme that catalyzes the reversible hydrogen evolution reaction/hydrogen oxidation reaction (HER/HOR), 2H⁺ + 2e⁻ ↔ H₂. They have been subject of many investigations not only for their biological significance in the metabolism of anaerobic bacteria, but also for their possible application in future energy technologies. Hydrogenase in bacteria, for example, can be used to catalyze the production of viable quantities of hydrogen for fuel. Under optimal conditions, one hydrogenase molecule has been shown to catalyze the production of 6000–9000 hydrogen molecules per second [1, 2]. Hydrogenase has also been considered to catalyze the HOR in fuel cells [3–5] which at present requires the precious metal platinum.

The structures of Fe-only hydrogenase from Clostridium pasteurianum and Desulfovibrio desulfiticans determined by X-ray diffraction techniques have been reported by Peters et al. [5] and Nicolet et al. [6]. Common to both X-ray diffraction results is the presence of 4Fe4S iron sulfur clusters linked to the [2Fe]₄ sub-cluster (Fig. 1(a)) active site—a diiron center with CO and CN- ligands linked through a putative 1,3-propanedithiolate. In this paper, we report the electronic structure of two hydrogenase analogues by density functional theory. Results are compared with electron affinities and molecular orbital energies obtained by gas-phase photodetachment photoelectron spectroscopy (PES) in the previous work by Yang et al. [7]. While PES is an outstanding tool to study the electronic structure, we are re-visiting these results due to the current availability of more sophisticated computational tools. Electron affinity, a measure of ion and free radical stability, is important in the electronic transfer and reactions of biological processes. An accurate description of the electronic structure of the 2Fe₃S hydrogenase analogues is of key importance in our efforts to design new HER/HOR catalytic materials.

II. CALCULATIONS

We modeled and performed spin-restricted density functional theory (DFT) calculations on compounds [(i-PDT)Fe₂(CO)₄(CN)]²⁻ (compound I) and...
\[\text{Fe}_2(\text{CO})_4\text{MeSCH}_2\text{C}((\text{Me})-(\text{CH}_2\text{S})_2(\text{CN}))^{-1}\] (compound II) in the singlet ground state as implemented in GAUSIAN 03 [8]. While there were actually five compounds studied by Yang et al. [7], three were not considered due to the similarity of their bonding at the iron centers and of their PES experimental results to the two compounds studied herein. Full geometry optimization was performed using 6-31+G(d,p) with the three parameter Becke/Lee-Yang-Parr (B3LYP) hybrid DFT functionals [9] and Becke/Perdew-Wang (BPW91) pure DFT functionals [10] for our exchange-correlation functionals. For single-point energy calculations, calculations were also performed with 6-31++G(d,p), 6-311++G(d,p) basis sets with B3LYP and BPW91.

For electron affinity (EA), or more precisely the adiabatic detachment energy (ADE), spin-unrestricted single point energy calculations were performed on [(i-PDT)\text{Fe}_2(\text{CO})_4(\text{CN})_2]^{-1}\text{ and }[\text{Fe}_2(\text{CO})_4\text{MeSCH}_2\text{C}((\text{Me})-(\text{CH}_2\text{S})_2(\text{CN}))^{-1}\text{] based on the relaxed geometry obtained for [(i-PDT)\text{Fe}_2(\text{CO})_4(\text{CN})_2]^{-2}\text{ and }[\text{Fe}_2(\text{CO})_4\text{MeSCH}_2\text{C}((\text{Me})-(\text{CH}_2\text{S})_2(\text{CN}))^{-2}\text{]. Geometry optimization was not performed in consideration of the Franck-Condon factor. Electron affinity is computed as: \(E_{\text{A}} = E(\text{optimized anion}) - E(\text{single-point calc. anion+1})\) [11].

III. RESULTS AND DISCUSSIONS

We compare the ADE from our DFT calculations with PES data as shown in Table 1. We found that 6-311+G(d,p) yields result comparable to the bigger 6-311++G(d,p) basis sets. B3LYP exchange and correlation functionals tend to slightly underestimate the EA, while BPW91 tends to slightly overestimate it. With spin unrestricted calculations however, spin unrestricted calculation was significantly larger for B3LYP (-16%) than BPW91 (-2%). All results are well within the expected ±0.2 eV of the experimental value [11] of 1.5 and 3.3 eV for compounds I and II, respectively.

The molecular orbital energies from our BPW91/6-311+G(d,p) calculation are now reported. Molecular orbitals obtained with smaller basis sets [BPW91/6-31+G(d,p) and B3LYP/6-31+G(d,p)] do not show significantly different results for spin restricted systems, while molecular orbitals of the bigger basis set cannot be retrieved due to memory limitations. Nevertheless, our results and the PES data obtained by Yang et al. showed consistent trends. Specifically, energy regions of molecular orbitals in our calculation corresponds well to the bands in the PES spectra, and energy gaps with no molecular orbitals present coincides well with valleys in the PES spectra. The energy of the molecular orbitals and their corresponding regions in the PES are shown in Table 2. For compound I, the near HOMO levels cannot be seen in the PES because they are positive values. For compound II, the near HOMO region can be seen as predicted our DFT calculations in the PES but the signal is weak indicating the wavelength (157 nm) used could too high for this region.

Wave functions of the HOMO and LUMO are plotted in Fig. 2. As can be seen in the figure, electrons in each orbital are delocalized between the iron centers and the ligands. The Fe-Fe bonding and anti-bonding are still clearly seen for the HOMO and LUMO respectively as described for \(\text{Fe}_2\text{S}_2\text{CO}_6\) clusters [12]. The other near HOMO-LUMO wave functions (not shown) all possessed iron properties; orbitals with predominantly ligand characteristics are not seen.

In compound II, it can be seen that HOMO electrons also cover the terminal sulfur. This corroborates the works of Scwab et al. [13] that the \(\text{[Fe}_2\text{]}\) subcluster and the neighboring \(4\text{Fe4S}\) cluster found in biological systems, should actually be designated as an electronically inseparable 6Fe6S. This, however, does not imply that only \(\text{[Fe}_2\text{]}\) subcluster analogues with \(4\text{Fe4S}\) analogues will be catalytically active to HER/HOR; indeed, Gloaguen et al. [14] has also shown that replacing a cyanide group in compound I with \(\text{CH}_3\text{P}\) results in a catalytically active compound.

The HOMO energy of compound I is much higher than that of compound II, which is understandable because compound I is in the \(-2\) anionic state while -1 for compound II. To compare the effects of ligands—specifically, a second CN versus a terminal sulfur ligand—results for compound I after one electron is removed [(i-PDT)\text{Fe}_2(\text{CO})_4(\text{CN})_2]^{-1}\text{ or “compound I-1e”} were compared with compound II. We found that compound I-1e has a much lower HOMO at \(-3.7\) eV versus \(-1.43\) eV for compound II, even if their 2Fe centers have the same oxidation states. Mulliken charge analysis also shows that the terminal sulfur has a stronger electron donating effect than CN ligand with 2Fe charges of 4.88 for compound I and 4.66 for compound II.

From the standpoint of computational materials design, it can be seen that changing ligands will primarily affect the electron affinity, charge distribution and HOMO/LUMO wave function/energy levels of \(2\text{Fe2S}\) clusters. We therefore think that similarities in electron affinity, 2Fe charge density and HOMO/LUMO characteristics to the biologically present active site should actually be designated as an electronically inseparable 6Fe6S. This, however, does not imply that only \(\text{[Fe}_2\text{]}\) subcluster analogues with \(4\text{Fe4S}\) analogues will be catalytically active to HER/HOR; indeed, Gloaguen et al. [14] has also shown that replacing a cyanide group in compound I with \(\text{CH}_3\text{P}\) results in a catalytically active compound.
drogenase is important for future energy technology. In this study, we show the electronic properties of hydrogenase analogues [(i-PDT)Fe₂(CO)₆(CN)]²⁻ (compound I) and [Fe₂(CO)₄MeSCH₃C(Me)-(CH₂S)₂(CN)]⁻ (compound II) by density functional theory and compare our results with photoelectron spectroscopic data. BPW91/6-311+G(d,p) shows good agreement with experimental electron affinity data while B3LYP shows significant spin contamination. The features of the PES spectra are consistent with the energy levels of the molecular orbitals. The HOMO orbitals show the familiar Fe-Fe bonding characteristics while the LUMO shows the Fe-Fe antibonding characteristics. In compound II, it can be seen that HOMO electrons also cover the proximal sulfur.

To compare the effects of ligands—specifically, a second CN versus a terminal sulfur ligand—we compare our results for compound I after one electron is removed [(i-PDT)Fe₂(CO)₄(CN)]⁻ to the data for compound II where one CN has been replaced by a terminal sulfur. We found that HOMO electrons also cover the proximal sulfur.

From the standpoint of computational materials design, we therefore think that similarities in electron affinity, 2Fe charge density and HOMO/LUMO energy to the biologically present active site should be bases for predicting catalytic activity.
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