Theoretical Evidence of Solvent-Mediated Excited-State Dynamics in a Functionalized Iron Sensitizer

The solvent-mediated excited-state dynamics of the COOH-functionalized Fe-carbene photosensitizer \([Fe(bmicp)_2]^{2+}\) \((bmicp = 2,6\text{-bis(3-methyl-imidazole-1-ylidine)-4-carboxy-pyridine})\) is studied by time-dependent density functional theory, as well as classical and quantum dynamics simulations. We demonstrate the crucial role of the polar acetonitrile solvent in stabilizing the metal-to-ligand charge transfer (MLCT) states of the investigated molecule using the conductor polarizable continuum model. This leads to dynamics that avoid sub-ps back electron transfer to the metal and an exceptionally long-lived 1MLCT state that does not undergo sub-ps 1MLCT \(\rightarrow\) 3MLCT intersystem crossing as it is energetically isolated. We identify two components of the excited-state solvent reorganization process: an initial rotation \((\sim 300\text{ fs})\) and diffusional dynamics within the local cage surrounding the rotated solvent molecule \((\sim 2\text{ ps})\). Finally, it is found that the relaxation of the solvent only slightly affects the excited-state population dynamics of \([Fe(bmicp)_2]^{2+}\).
Dissociation, absorption and ionization of some important sulfur oxoanions (S\textsubscript{2}O\textsuperscript{2-} \(n = 2, 3, 4, 6, 7\) and 8)

Abstract In this work, a systematic theoretical study was performed on the dissociation, absorption and ionization of several important sulfur oxoanions (S\textsubscript{2}O\textsuperscript{2-} \(n = 2, 3, 4, 6, 7\) and 8)). \(\Delta E_{\text{elec}}\) (thermal corrected energy), \(\Delta H^o\) and \(\Delta G^o\) of the dissociation reactions of the oxoanions to their radical monoanions were calculated using combined computational levels of theories such as Gaussian-3 (G3) and a new version of complete basis set method (CBS-4M) in different environments including gas phase, microhydrated in gas phase and different solvents. Calculations showed S\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} is the most stable anion against the dissociation to its radical monoanions (SO\textsubscript{4}\textsuperscript{-} + SO\textsubscript{3}\textsuperscript{-}). It was also found that S\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} has more tendency to dissociate to its radical anions (SO\textsubscript{2}\textsuperscript{-} + SO\textsubscript{2}\textsuperscript{-}) compared to the other anions. The absorption spectra of the anions were also calculated using the time-dependent density functional theory (TD-DFT) employing M062X functional. The effect of microhydration and electrostatic field of solvent on the different aspects (intensity, energy shift and assignment) of the absorption spectra of these anions were also discussed. It was observed that both hydrogen bonding and electrostatic effect of water increases the intensity of the absorption spectrum compared to the gas phase. Effect of microhydration in shifting the spectra to the shorter wavelength is considerably higher than the effect of electrostatic field of water. Finally, several gas phase ionization energies of the anions were calculated using the symmetry-adapted cluster-configuration interaction methodology (SAC-CI) and found that the first electron detachment energies of S\textsubscript{2}O\textsubscript{2}\textsuperscript{-}, S\textsubscript{2}O\textsubscript{3}\textsuperscript{-} and S\textsubscript{2}O\textsubscript{4}\textsuperscript{-} are negative. Natural bonding orbital (NBO) calculations were also performed to assign the electron detachment bands of the anions.

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Prediction of acidity constants of some important selenium oxoacids in aqueous solution by computational techniques

The acidity constants ($pK_a$) of two important series of selenium oxoacids including $\text{H}_2\text{SeO}_n$ ($n = 1-5$) and $\text{H}_2\text{Se}_2\text{O}_n$ ($n = 1, 3, 4, 6$ and $7$) were predicted by using two different computational methods for the first time. The calculations were performed using MP2 level of theory employing a very large basis set, 6-311++G(3df,3pd), and a new density functional method, M06-2X, with the same basis set, separately. A new continuum solvation model, SMD, based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent, was used to account the solvent effects. The calculated values of $pK_a$ were corrected using the different correlation equations, reported in the literature, to improve the accuracy of results. Also, the calculated results in this work were compared with the corresponding results related to sulfur oxoacids obtained in our previous work. The same trend was observed for the variation of the acidity constants of selenium oxoacids and corresponding sulfur oxoacids (with the number of oxygen atoms). Comparison of the $pK_a^1$ of selenium and sulfur oxoacids showed that the acidity strength of sulfur is higher than selenium while for $pK_a^2$, selenium oxoacids are stronger acids than sulfur oxoacids. The predicted values of $pK_a$ of selenium oxoacids are important and useful in the different chemical aspects of these compounds in chemistry and biochemistry.

General information

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BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 3.87 SJR 1.113 SNIP 0.962
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Scopus rating (2013): CiteScore 3.74 SJR 1.119 SNIP 0.904
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Scopus rating (2012): CiteScore 2.4 SJR 0.872 SNIP 0.619
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Acidity constants of some sulfur oxoacids in aqueous solution using CCSD and MP2 methods

The calculations of the acidity constants (pKₐ) of a series of sulfur oxoacids including H₂SOₙ (n = 1-5) and H₂S₂Oₙ (n = 1, 3, 4, 6 and 7) are presented for the first time. The calculations were performed using two expensive correlated levels of theory including MP2/6-311++G(3df,3pd) and CCSD/6-311++G(d,p) in both gas and aqueous phases. The new continuum solvation model, SMD, based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent, used to account the solvent effects. The calculated pKₐs were corrected using the different correlation equations (Zimmermann and Tossell, J. Phys. Chem. A, 2009, 113, 5105-5111) to improve the accuracy of results. Also, the calculated results showed the effect of the intramolecular hydrogen bonding on the acidity strength.
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Web of Science (2012): Indexed yes
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Scopus rating (2011): CiteScore 3.68 SJR 1.163 SNIP 0.751
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Web of Science (2005): Indexed yes
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Theoretical studies on the tautomerism of tetrazole selenone
The tautomerism of all possible forms of tetrazole selenone (A-G), induced by proton transfer, was studied, theoretically, in different environments including gas phase, continuum solvent and microsolvated environment with one or two explicit water or ammonia molecules. The calculations were performed using two different levels of theory including mPW2PLYP and DFT-B3LYP. The 6-311++G(d,p) basis set was used for C, H, O and N and the standard relativistic effective core pseudo potential LANL2DZ basis set was used for Se atom. It was found that the tetrazole selenone, in the form of A, is the most stable isomer in all of the environments considered in this work. The kinetics of proton transfer reaction was studied in both gas and solvent environments and it was concluded that the activation energy of the reaction increases with going from the gas phase to polar solvents. Moreover, the proton transfer reaction assisted by one or two water or ammonia molecules was investigated and it was found that the activation energy significantly reduces.

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Theoretical study on the mechanism and kinetics of acetaldehyde and hydroperoxyl radical: An important atmospheric reaction

A systematic theoretical study was performed on the mechanism and kinetics of the atmospheric reaction of acetaldehyde (CH$_3$CHO) and hydroperoxyl radical (HO$_2$) in the gas phase. The DFT-B3LYP/6-311++G(3df,3pd) and CCSD(T)/6-311++G(d,p) methods were employed for calculations. Based on the calculations, this reaction leads to four different
products through radical addition and hydrogen abstraction mechanisms which are very important in atmospheric and combustion chemistry. The favorable reaction paths begin with α-hydroxyethylperoxy radical, CH$_3$CH(OO)OH, in an exothermic process and finally leads to the product P1 (CH$_3$COOH + OH). The overall rate constants for favorite reaction paths have been calculated at different temperatures (200–2500 K).

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BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.213 SNIP 0.932
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Theoretical study on the structures, stabilities and electronic properties of S$_2$O$_5^{2-}$ isomers in the gas and solution phases

Different theoretical levels of theory including B3LYP/6-31+G(3df,3pd), MP2/6-311+G(3df,3pd), QCISD/6-311+G(d,p), CBS-QB3 and CCSD(T)/6-311+(d,p)//B3LYP/6-311+G(3df,3pd) have been employed to determine the structures, relative stabilities, electronic properties and thermochemistry of the selected S$_2$O$_5^{2-}$ isomers in the gas phase and aqueous solution. Atoms in molecules (AIM) method and natural bonding orbital (NBO) were used to characterize the origin of atomic bonds. The NBO and AIM calculations showed that the strength of S-O and S-S bonds in the (O$_3$SSO$_2$)$_2^-$, (O$_2$SOSO$_3$)$_2^-$ and (OSOSO$_3$)$_2^-$ isomer are relatively weak and go toward dissociation to form SO$_3$-, SO$_2^-$, SO$_3^-$, SO$_4^{2-}$ and SO$_4^{3-}$ radical anions. For more confirmation, the dissociation equilibrium constant ($K_{diss}$) of each isomer were calculated at 298K and showed that by increasing the dielectric constant of the solvent, the stability of the S$_2$O$_5^{2-}$ isomer increases. Based on these result, the isomers are considerably unstable and dissociate in the gas phase compared with solution.

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Projects:

Atomistic Mechanisms of Functional Molecules
Abedi, M., PhD Student, Department of Chemistry
Møller, K. B., Main Supervisor, Department of Chemistry
Henriksen, N. E., Supervisor, Department of Chemistry
Pápai, M. I., Supervisor, Department of Chemistry
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