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A New Modification of Morse Potential Energy Function

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ABSTRACT

Interaction of meso – tetrakis (p-sulphonato phenyl) porphyrin (hereafter abbreviated to TSPP) with Na+ has been examined using HF level of theory with 6-31G* basis set. Counterpoise (CP) correction has been used to show the extent of the basis set superposition error (BSSE) on the potential energy curves. The numbers of Na+ have a significant effect on the calculated potential energy curve (including position, depth, and width of the potential well).

Keywords: Potential energy, Morse function, Ab initio; BSSE; TSPP

INTRODUCTION

One possible way to obtain an intermolecular interaction potential is to use several experimental data to optimize parameters of a proposed potential function. The difficulty of this method is primarily that experimental measurements can indicate only about a limited region of the potential energy surface. In particular, the shape of an anisotropic potential is impossible or very difficult to be derived from experiments.

Another way to obtain an intermolecular potential is made available by quantum chemistry. Using quantum chemical methods, detailed information about the interaction energy over a wide area of the potential surface can be derived. However, apart from the simplest systems , one has to use some level of approximation in quantum chemical calculations. Poor approximations, mainly forced by limited computing facilities, can cause serious deficiencies of the calculated potential points [1]. Therefore, it is only by using chemical judgment that one can combine information from different sources to produce a satisfactory function for the whole surface.

Chemistry is a dynamical process with interactions between molecules and atoms dependent on the forces F(r) between the atoms:

$$F(r) = -dV(r)/dr \quad (1)$$

To understand the dynamics of a chemical system we need to understand all the forces operating within the system, hence we need to know V (r). In a multi-dimensional system V (r) is known as the potential energy surface. The

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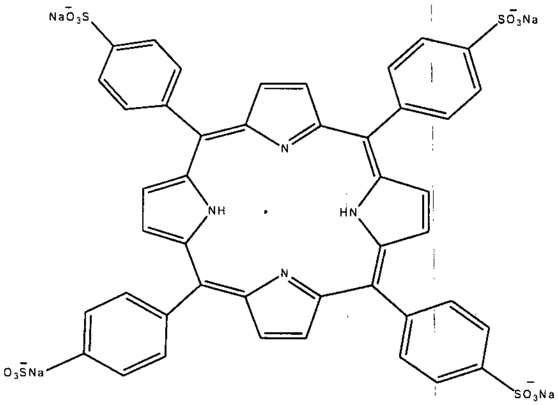
potential energy surface (PES) is typically defined within the Born Oppenheimer approximation: electrons are much lighter than nuclei, thus they move much faster and adjust adiabatically to any change in nuclear configuration. This means that a separate PES is defined for each possible electronic state. Generally, the dynamics are studied on the ground electronic state surface. Unless stated otherwise the discussion here is for the ground electronic state surface (This is also known as the electronic adiabatic approximation).

For a nonlinear molecule, consisting of N atoms, the potential energy surface depends on 3N-6 independent coordinates, and depicts how the potential energy changes as relative coordinates of atomic nuclei involved in the chemical reaction are varied. An analytic function which represents a potential energy surface is called a potential energy function. Understanding the relationship between properties of the potential energy surface and the behavior of the chemical reaction is a central issue in chemical kinetics. Both the macroscopic thermal rate constant for a chemical reaction and its microscopic counterpart such as a quantum mechanical state-to-state reaction probability may be interpreted in terms of a potential energy surface.

Owing to their multifunctional structure and complex formation abilities, porphyrines play not only a very important role in metabolic processes, but a number of the chemical features of this category of compounds can be exploited in analytical chemistry as well[2,3].

This paper reports a study on interaction of (meso – tetrakis (p-sulphonato phenyl) porphyrin (hereafter abbreviated to TSPP) (Scheme 1) with one, two, three and four Na^+ respectively. Porphyrines represent an interesting family of compounds used now for the photodynamic therapy (PDT) of malignant tumors [4, 5]. Porphyrines have attracted large attention because of their role in the human body, ability to accumulate in many kinds of cancer cells, as well as magnetic and optical properties. These features make them useful in cancer medicine and photodynamic therapy [6].



Scheme1 .Tetra sodium meso – tetrakis (p-sulphonato phenyl) porphyrin (TSPP).

THEORY AND METHODS OF THEORETICAL CALCULATION

Initially, structure of TSPP was fully optimized with the HF method and 6-31G* basis set in order to locate the stationary points on the potential surface. Our calculations were performed by using the program package Gaussian 98[7].

In ab initio calculations the basis set superposition error (BSSE) is of paramount importance. This error can be eliminated to some extent by using the counterpoise method (CP). The interaction energy, V, for two open shell A and B systems can simply be given as

$$V=E_{AB}\,(A---B) - E_{AB}\,(A+B) \qquad (2)$$

where the arguments in parenthesis indicate the basis set being used. E_{AB} (A---B) is the energy of the A---B system at the r distance while E_{AB} (A+B) is the energy of the two isolated components, at infinity ($r=\infty$).In ab initio calculation the basis set superposition error (BSSE) is of paramount importance [8].This error can be eliminated to some extent by using the counterpoise method (CP) [9,10]. In this method both the physicochemical compound A---B and the A and B components at $r=\infty$ are calculated by using the full basis set for the A---B, hence

$$V=E_{AB}(A---B) - E_{AB}(A+B) + \Delta E_{CP} \qquad (3)$$

where

$$\Delta E_{CP} = [E_A\,(A+B) - E_A\,(A---B)] + [\,E_B(A+B) - E_B\,(A---B)] \qquad (4)$$

Using quantum chemical methods, detailed information about the interaction energy over a wide area of the potential surface can be derived. This approach can be used to extract detailed information of the potential energy surface, which is sometimes difficult or practically impossible by other methods. The basis set superposition error has a significant effect on the calculated interaction potential and therefore it should be corrected [11].

The significant of the BSSE on the intermolecular interaction has been highlighted in a number of papers [12, 13] .The various points on the ab initio potential energy surface were used to obtain a fit to the Lennard – Jones and Morse and Morse modified potential energy function.

RESULTS AND DISCUSSION

We calculated the intermolecular interaction energies of the TSPP with one, two, three and four Na^+ respectively. The intermolecular potential energy interaction obtained at HF level of theory with the basis set 6-31G* that plotted in figure 1as function of r; the distance between TSPP and Na^+. Calculated potential energy curves, including position, depth and width of potential well were shown in figure1.

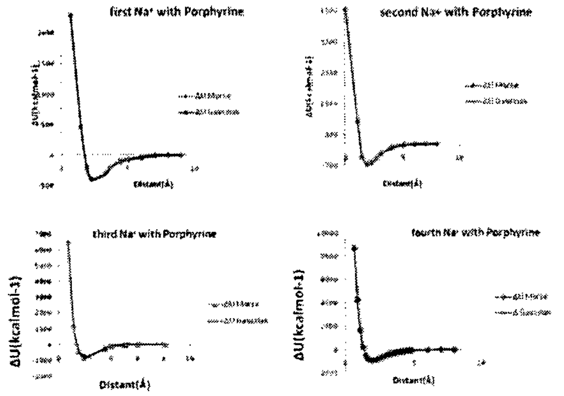


Figure1. Interaction energy between TSPP and Na^+ by the modified Morse function and Gaussian calculations.

Most of the popular approximation such as, for instance, the Lennard-Jones potential and the exp-6 potential and Kihara potential yielded unsatisfactory results. Finally, we have chosen the six-parameter generalized Morse modified function [14].

$$U(r) = D_e \{1 - \exp[-\beta(r - r_e)] - 1\}^2 \qquad (5)$$

D_e ,β, r_e are positive and usually chosen to fit the bond dissociation energy, the harmonic vibration frequency and the equilibrium bond length. The results of search are shown in table1.

Table 1. The values of D_e ,β and r_e after fitting

Parameters / Interaction	D_e (kcal/mol)	B (Hz)	r_e (Å)
$1Na^+$ & TSPP	396.63	0.95	2.05
$2Na^+$ & TSPP	661.44	-1.06	1.94
$3Na^+$ & TSPP	772.40	-1.12	1.96
$4Na^+$ & TSPP	902.79	-1.14	1.97

The calculated potential energy surface can be compared based on the values of the position of the minimum point (re) of the potential curves. As is evident from table 2, these quantities are very sensitive to the number of metal used in the computations. In ab initio calculations the basis set superposition error is of paramount importance. BSSE corrected TSPP – Na+ intermolecular potential energy curves corresponding to those calculated, are plotted against r in figure1. In this figure the values of UG (calculated by Gaussian) and UM (calculated by Morse modified function are fitted by Excel) are shown. The values of UG (calculated by Gaussian program) and UM (calculated by Morse modified function) and r are shown in table 2.

Table2.The values of U_G (calculated by Gaussian program) and U_M (calculated by Morse modified function) and r

# of Na^+	r(Å)	U_M (kcal/mol)	U_G (kcal/mol)	r(Å)	U_M (kcal/mol)	U_G (kcal/mol)	r(Å)	U_M (kcal/mol)	U_G (kcal/mol)
1 Na^+	0.7	2287.5482	2281.4090	3.3	-295.1782	-307.5424	6.0	-47.4405	-27.8594
	1.5	457.0539	471.7570	3.6	-206.7144	-206.4924	7.0	-18.7844	0.5232
	1.9	-207.7790	-198.0840	4.4	-116.0221	-90.1452	8.0	-7.3498	0.9820
	2.3	-386.7621	-403.2033	5.0	-81.6385	-59.2142	9.0	-2.8628	0.2367
2 Na^+	0.7	4314.1224	4308.7336	2.3	-593.8583	-616.7155	5.0	-49.6983	-36.4868
	1.1	717.4139	732.7046	2.7	-457.1438	-461.0516	6.0	-17.3413	0.2566
	1.5	-426.7134	-418.2615	3.1	-328.0764	-315.6525	7.0	-6.0005	0.8926
	1.9	-660.2824	-656.0569	4.0	-138.8944	-126.5186	8.0	-2.0704	0.0000
3 Na^+	0.7	6577.9126	6577.9794	2.3	-694.6552	-731.6967	6.0	-16.7532	0.5695
	1.1	1234.2485	1237.854	3.5	-251.0915	-232.8225	8.0	-1.7991	0.0000
	1.5	-425.6992	-461.9022	4.0	-149.5865	-105.1112			
	1.9	-768.8564	-675.5745	5.0	-50.6696	28.4875			
4 Na^+	0.7	8704.7362	8695.8911	2.4	-765.3076	-845.2531	4.0	-167.9594	-123.5944
	0.9	4256.9292	4271.5012	2.6	-663.4195	-652.8084	4.2	-135.0255	-94.1098
	1.1	1698.1193	1659.6326	2.8	-562.3175	-557.4721	4.4	-108.3454	-41.1908
	1.3	282.155	344.1444	3.0	-469.2026	-455.9625	4.6	-86.7175	-20.1862
	1.5	-451.5135	-404.0413	3.2	-387.0986	-358.4645	4.8	-69.3416	-30.5395
	1.6	-656.3055	-666.7182	3.4	-316.7024	-341.9554	6.0	-17.8369	-10.2545
	1.8	-862.5213	-891.2254	3.6	-257.4858	-192.2522	7.0	-5.7022	0.2492
	2.0	-901.5854	-940.5145	3.8	-208.3422	-142.9425	8.0	-1.8187	0.0000
	2.2	-853.5655	-894.9094						

CONCLUSION

Calculated potential energy curves, including position, depth and width of potential well were also shown in figure2. The calculated potential energy surface can be compared based on the values of the position of the minimum point (r_e) of the potential curves. These quantities are very sensitive to the number of metal used in the computations. When four Na^+ are around the TSPP, this stable complex has a symmetry configuration and a minimum potential energy.

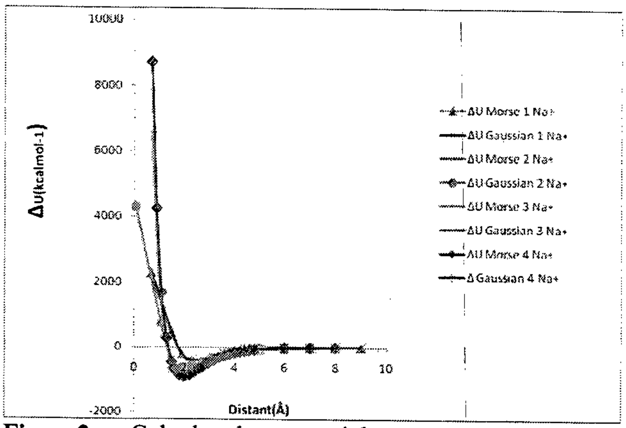


Figure2. Calculated potential energy curves, including position, depth and width of potential.

REFERENCES

1. S.Bock,E.Bich,E.Vogel,Chemical physics ,2000 257,147.
2. M. Biesaga, K.Pyrz 'n yska, M.Trojanowicz, Talant, 2000, 51,209-224
3. Z. Deyl, I.Miksik, A.Eckhardt, V.Kasicka and V.Kral, Current Analytical Chemistry, 2005, 1, 103-119.
4. E.A. Lukyanets, J. Russ. Chem. ,1998, 42, 9–16.
5. A.A.Chernonosov, N.A.Kuznetsov, V.V.Koval, D.V.Pyshnyi, N.M.Derkacheva, E.A.Lukyanets, O.S.Fedorova, Nucleosides, Nucleotides, Nucleic Acids, 2004, 6, 983.
6. M.I.Gaiduk, V.V.Grigryants, A.F.Mirnov, V.D.Rumyantsera, V.I.Ghissov, G.M.Sukhin, J.Photochem.Photobiol.B.Biol ,1990,7,15.
7. M.J. Frisch, et al. Gaussian 98, Revision A.3, Gaussian, Inc., Pittsburgh PA (1998).
8. B.Liu, A.D.McLean, Chem.Phys.1973, 59, 4557.
9. S.F.Boys, F.Bernardi, Mol.Phys.1970, 19,553.
10. M.Naroznik, Molecular structure, 2003,624,267.
11. S.F.Boys, F.Bernardi ,Mol.Phys., 1970,19,553.
12. F.B.van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt,J.H.van Lenthe, Chem.Rev.1994,94,1873
13. R.D.Parra, X.C.Zeng, Molecular structure, 2000,503,213.
14. W.L.Hase, S.L.Mondro, R.J.Duchovic, D.M.Hirst, J.Am.Chem.Soc. 1987, 109, 2916.