# Analysis of Complexes Pairing Performat Radical and Water

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*Abstract*—The present article comprises a theoretical study of structures Performat radical (HCO$_3$) with H$_2$O molecule. We make use of ab initio quantum chemical methods. Unrestricted Hartee-Fock (UHF) with the basis set6-311+g(2df,2p) and density functional theory (B3LYP) with the basis set 6-311+g(2df,2p) and also we done atoms in molecules (AIM) theory for them. We have found four stable geometries the PerformatRadical(HCO$_3$) with H$_2$O.

*Keywords*—Hydrogen binding, Performat Radical, Water, Gaussian, Atoms in molecules (AIM) theory

## I. INTRODUCTION

STUDIES of non-covalently bonded moleculer clusters are of certain interest for contemporary chemical science fromseveral both fundamental and applicative aspects[1]. Among all non-covalent interactions, the hydrogen binding ones are particularly significant. Although a rather large number of studies devoted to the hydrogen binding phenomenon has been published in the literature(from both experimental and theoretical viewpoints[1-5]), most of these studies have been devoted to hydrogen bonds formed in the case of complexes between neutral and ionic(often closed-shell) molecular systems and close-shell molecular systems. When interactions between open-shell systems (such as radicals) and closed-shell molecular systems is in question, the number of studies is much limited. This is due to both experimental and also theoretical difficulties arising in description and characterization of the systems in question. Having in mind the importance of free radicals in a number of fields of contemporary science (such as atmospheric chemistry, life sciences etc.), studies of the intermolecular interactions involving exactly these open-shell systems are highly desirable[6].

Peracids play a vital role in several chemically important reactions such as oxidizing agents in the epoxidation type ofreagent in Baeyer-Villiger oxidation type of reactions, and soforth[6]. However, until there where we know, there are no much theoretical of radical Performat with water. In the present study, we focus on possibility of formation of complex Performat radical and water (HCO$_3$---H$_2$O) in the

## II. PROCEDURE FOR PAPER SUBMISSION

### A. General Calculation Method

All calculations performed in this work have been carried out by using the Gaussian 03 program package[7]. The geometries of the monomers and complexes has been optimized at the 6-311+g(2df,2p) basis set[8] employing the unrestricted density functional Becke's two parameter and Lee-Yang-Parr functional (B3LYP) method[9].At this level of theory, we have also calculated the nature of the corresponding stationary points (minima or transition states) and to provide the zero-point vibrational energy (ZPVE). The interaction energy has been corrected from the inherent basis sets superpositions error (BSSE) using the full counterpoise method of Boys and Bernardi[ 10] at each calculated level, and also the AIM[11] anylyes of B3LYP were performed.The NBO[12] methodology allows us to study the bonding-antibonding orbital interactions and we are reported their results in Table II.

### B. Monomers

We have found two stable geometries the PerformatRadical(HCO$_3$). Both are planar, one in cis and the other in a trans configuration. But in this study we have only considerd the cis conformer (see Fig 1), which corresponds to the lowest energy minimum, and the results are only briefly discussed.
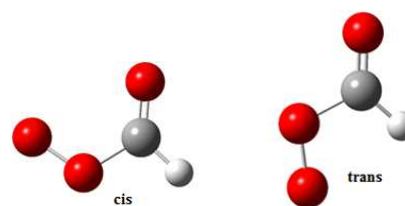


Fig. 1 Monomers

### C. Complexes

We have the four minima located on the surface of H$_2$Owith HCO$_3$ Radical with using B3LYP methodwhich they aredepicted in Figure 2.

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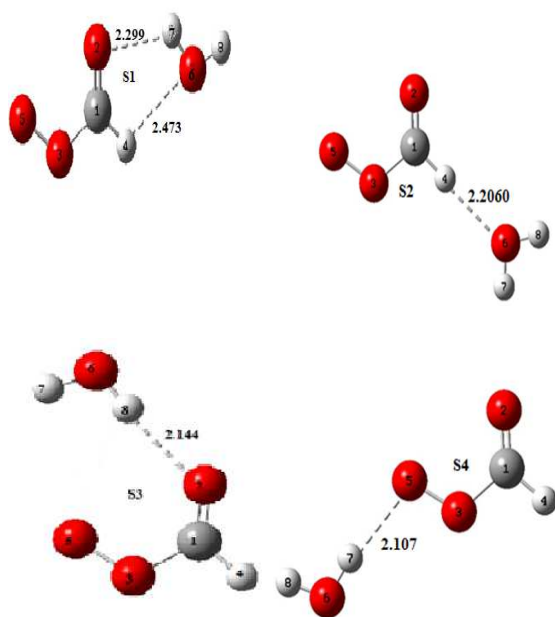
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Fig. 2 Complexes formed between $H_2O$ and $HCO_3$ Radical.

### III. RESULTS AND DISCUSSION

For the $H_2O$-$HCO_3$ complex, the most stable complexes studied in this work is complex 1, which has $C_1$ symmetry. Figure 2 shows that complex 1 has a five-member ring structure with one hydrogen bond, formed with the hydrogen of water and the oxygen carbonyl group($O_2H_7$) with a computed hydrogen-bond distance of 2.299 A° and the other bond formed between the oxygen of water and hydrogen Performat radical($O_6H_4$) with a computed length of 2.473 A°. Complex 3 has one hydrogen bonds, formed between the hydrogen of water and oxygen of carbonyl group ($O_2H_8$) with a computed hydrogen-bond distance of 2.144 A°. Complex S4 has also one hydrogen bond($O_5H_7$) with length of 2.107 A°, which it is the shortest bond among other structures. Inaddition, complexe S2 has no hydrogen bond however it has one bond between oxygen of water and hydrogen Performatradical($O_6H_4$) with a computed distance of 2.206 A°. The optimized geometries obtained by B3LYP method are displayed in Table I. The interaction energy is reported first without, and then with, counterpoise correction of basis set superposition error. The next two columns report these same quantities after the zero-point vibrational contributions have been added in. One may note that the ZPVE tends to diminish the binding energy by 4.5 – 5.5 kJ/mol, as does the counterpoise correction.( The only exception is the reversal between S3 and S4 in the $D_0^{cp}$ quantity). After full correction for the latter quantities, the interaction energy of the $H_2O$ + $HCO_3$6-311+g(2df,2p) level.complex S4 with one hydrogen bond has less stable than four structures.The figure 3 shows the atoms in molecules (AIM) theory and the value of electron density at BCP are given in Table III and IV. $CP_S$ are classified according to their spectrum, which is the set of eigenvalues of the Hessian matrix of electron density, $\{\lambda_1 \leq \lambda_2 \leq \lambda_3 \}$ [13,14]. The number of non-zero eigenvalues and their associated sign are sufficient to define the type of a CP. The BCP has two negative eigenvalues, $\lambda_1 \leq \lambda_2 \leq 0$, and one

positive eigenvalue, $\lambda_3 > 0$. The ellipicity at the BCP; For ellipicity which is defined as $\varepsilon = [\frac{\lambda_1}{\lambda_2} - 1]$ indicates the stability of the BCP with respect to small geometrical changes such as those occurring during molecular vibration[14]. In there, the values of ellipticity for the investigated molecules range from 0.342 in S1 to 0.0033 in S3. For the investigated molecules $\nabla^2\rho$ are positive, and range from 0.0024 in S1 to 0.3172 in S3 au, where at a BCP, $\nabla^2\rho > 0$ as in H-bonding interaction or in ionic bonds and $\nabla^2\rho < 0$ as in covalent [13,15,16] in each dimer. In this work, the values of $\nabla^2\rho > 0$ for all of the dimers. G at the BCP is the kinetic electron energy density, V at the BCP is the potential electron energy density[17], which in this work,$-G_{BCP}/V_{BCP}$ is greater than 1 and this indicates a noncovalent interaction for all of the structers.

TABLE I
BINDING ENERGIES (KJ MOL$^{-1}$) THERMODYNAMIC DATA FOR THE ASSOCIATION OF PERFORMAT RADICAL ($HCO_3$) WITH $H_2O$

| Entry | $D_e$ | $D_e^{cp, a}$ | $D_0$ | $D_0^{cp}$ |
|---|---|---|---|---|
| S1 | -16.5061 | -16.4546 | -11.0643 | -11.0129 |
| S2 | -15.3217 | -15.1864 | -11.6393 | -11.5040 |
| S3 | -11.8841 | -11.6011 | -6.7045 | -6.4215 |
| S4 | -10.3514 | -10.3788 | -5.4162 | -5.4437 |

TABLE II
BOND ANGLES, BOND STRETCHES. STRETCHING FREQUENCY SHIFTS AND CHARGE TRANSFERS FOR COMPLEXES PAIRING $HCO_3$ RADICAL WITH WATER

| S1 | | S2 | |
|---|---|---|---|
| θ ($O_6H_7O_2$),deg | 124 | θ ($O_6H_4C_1$),deg | 179 |
| θ ($O_6H_4C_1$),deg | 108 | Δr($C_1H_4$), mA° | 0.3 |
| Δr($O_6H_7$), mA° | 21.2 | q($O_6{\rightarrow}H_4$),me | 9.0 |
| Δr($C_1H_4$), mA° | 12.5 | Δν($CH_4$) | 8.44 |
| q($O_2{\rightarrow}H_7$),me | 3.8 | S4 | — |
| q($O_6{\rightarrow}H_4$),me | 1.5 | θ($O_6H_7O_5$),deg | 172 |
| Δν(C=O) | -23.07 | Δr($O_7H_6$), mA° | 6 |
| Δν($CH_4$) | 29.32 | Δr($O_3O_5$), mA° | 13.3 |
| Δν($O_6H_7$) | -26.45 | q($O_5{\rightarrow}H_7$),me | 12 |
| S3 | | Δν($O_5O_3$) | 15.03 |
| θ($O_6H_8O_2$),deg | 174 | Δν($O_6H_7$) | -51.81 |
| Δr($O_6H_8$) | 5.1 | — | — |
| q($O_2{\rightarrow}H_8$),me | 6.2 | — | — |
| Δν(C=O) | -11 | — | — |

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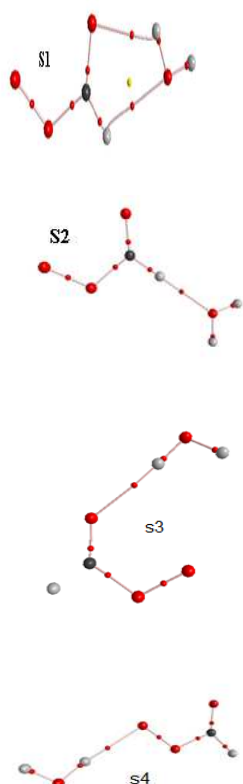International Journal of Nuclear and Quantum Engineering
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Fig. 3 Complexes formed between $H_2O$ and $HCO_3$ Radical with AIM theory

TABLE III
PARAMETERS FOR BONDS BETWEEN $H_2O$ AND $HCO_3$ RADICAL

| | Entry | $\rho_{BCP}$ | $\nabla^2\rho$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ |
|---|---|---|---|---|---|---|
| S1 | $H_7$--O=C | 0.0123 | 0.0029 | -0.0130 | -0.0111 | 0.0701 |
| | $H_4$--$O_6$ | 0.0089 | 0.0024 | -0.0079 | -0.0059 | 0.0522 |
| S2 | $H_4$--$O_6$ | 0.0145 | 0.0030 | -0.0172 | -0.0156 | 0.0812 |
| S3 | $H_8$--O=C | 0.0142 | 0.3172 | -0.0169 | -0.0169 | 0.0846 |
| S4 | $H_7$--$O_5$ | 0.0174 | 0.0034 | -0.0225 | -0.0213 | 0.0976 |

TABLE IV
PARAMETERS FOR BONDS BETWEEN $H_2O$ AND $HCO_3$ RADICAL

| | Entry | $\varepsilon$ | $G_{BCP}$ | $V_{BCP}$ | $-G_{BCP}/V_{BCP}$ |
|---|---|---|---|---|---|
| S1 | $H_7$--O=C | 0.1634 | 0.0106 | -0.0096 | 1.0960 |
| | $H_4$--$O_6$ | 0.3420 | 0.0078 | -0.0059 | 1.3114 |
| S2 | $H_4$--$O_6$ | 0.1044 | 0.0112 | -0.0102 | 1.0926 |
| S3 | $H_8$--O=C | 0.0033 | 0.0117 | -0.0107 | 1.0942 |
| S4 | $H_7$--$O_5$ | 0.0590 | 0.0134 | -0.0133 | 1.0066 |

## IV. CONCLUSION

Calculation at the UHF and B3LYP level, carried out in this work on Perform at radical and water have led us to the following conclusion. There are four minima on the potential energy surface of HCO3…H2O dimer. In the stablest structures, there are two interaction between H2O molecule and Performat radical (HCO3) and that has total energy about 16 kJ mol$^{-1}$ , reduced to 11 kJ mol$^{-1}$ when zero point vibrational energy is included. The C-H covalent bond is contracted when it participate in CH…O intraction, and its strectching frequency shifted to the blue, about 30 cm$^{-1}$, and the C=O…H interaction, and its stretching frequency shifted to the red, about -23 cm$^{-1}$. And also electron density analyses carried out for each H-bond.

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