# Hardness and Polarizability Profiles for Intramolecular Proton Transfer in Water Dimer Radical Cation

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In view of the recently reported discrepancies in the prediction of minimum energy structure (proton-transferred vs hemibonded) for the water dimer on ionization, we have performed complete active-space self-consistent field calculations followed by total energy evaluation using multiconfigurational quasi-degenerate perturbation theory to obtain very accurate relative energies of different structures and predicted the proton-transferred structure to be the most stable ones. The variations of hardness, polarizability, chemical potential, and energy for the proton-transfer process in this weakly interacting system (ionized water dimer species) are investigated through calculations using Hartree−Fock theory. It is observed that the transition state corresponding to the proton-transfer process is associated with maximum polarizability at different O−O distances for the water dimer cation, although the hardness minimum does not exactly correspond to the transition state. However, the hardness profiles scaled suitably with chemical potential are found to have minima at the transition states.

## 1. Introduction

In the last two decades, the qualitative concepts of electronegativity[1] and hardness,[2] which have been widely used intutively by chemists to rationalize and predict various aspects of chemical binding and reactivity of molecules, have been rejuvenated mainly because of two important developments in this area. The concept of electronegativity has been provided with a rigorous foundation[3] using the framework of density functional theory[4] (DFT), and a new quantitative definition of hardness[5] has been proposed. Defined, respectively, as the first-[6] and second-derivatives[5] of energy ($E$) with respect to the number of electrons ($N$), these two parameters essentially determine the response of an atom or molecule to the change in the number of electrons at fixed external potential, $v(\mathbf{r})$. The alternative response function corresponding to the change in the external potential at fixed $N$ defines the polarizability. An interconnection[7,8] between these two different response functions corresponding to changes in $N$ and $v(\mathbf{r})$, respectively, has now been established through DFT, and efficient schemes[8] for simultaneous calculation of the polarizability and hardness parameters have been proposed. The inverse relation of hardness and polarizability, in fact, has been well-known,[9,10] and recently, maximum hardness[12] as well as minimum polarizability[13,14] have been associated with greater stability of a species.

Although the qualitative concepts of hard and soft acids and bases have existed almost for thirty years, it is the quantification of these concepts that has rejuvenated[15−36] this area of research. The concept of hardness has attracted renewed attention for the study of chemical reactions after the discovery of the principle of maximum hardness,[12] and it has been shown[17−36] that the hardness profile along a reaction path passes through a minimum near or at the transition state for various types of reactions such as inversion, exchange, deformation, and isomerization. Along the lines of maximum hardness, there is already indication for a principle of maximum molecular valency.[19,35] For example, recent studies have shown[19,35] that the molecular valency reaches its minimum value at the transition state for isomerization type of reactions and maximum value at the equilibrium configuration for normal modes of vibrations and internal rotations. The correspondence between the variations of hardness, polarizability, molecular valency, and various energy components has also recently been investigated as a function of the reaction coordinate or the bond distortion in simple molecules.[13,19−22] Interesting correlations between electronegativity, hardness, polarizability, and size have also been shown[9,10] to exist.

Thus, insight into many processes has been obtained through the study of hardness profiles along the corresponding reaction coordinates. Thus, it is worthwhile to investigate other systems and processes for which the applicability and utility of such studies have remained unexplored. One of such interesting areas that will be of importance involves weakly interacting systems, as arising, for example, in hydrogen bonding in simple situations.

Understanding the nature of the hydrogen bond has been the subject of increasing research activities[37−40] in recent years because of its importance in many chemical and biological systems and processes, and in the crystal packing of many organic and organometallic compounds. The essence of the physical interactions that contribute to hydrogen bonds has been the subject of numerous discussions in the literature. Even the nature of interactions involved in an O−H···O hydrogen bond sometimes becomes controversial.[41,42] While the neutral hydrogen-bonded complexes, and in particular the water dimer $(H_2O)_2$, have been extensively studied theoretically, much less work has been done on the electronic and molecular structures of the corresponding radical cations. It is to be noted that ionized hydrogen-bonded systems exhibit a very rich and varied chemistry because in the ionized state they can evolve via different chemical reactions such as electron transfer, proton transfer, or molecular rearrangements. For the $(H_2O)_2^+$ system, theoretical studies based on post-Hartree−Fock methods have shown that the proton-transferred $(OH−H_3O)^+$ isomer is the ground state. Figure 1 shows the structures of neutral water dimer and the two isomers of $(H_2O)_2^+$ that can be obtained after

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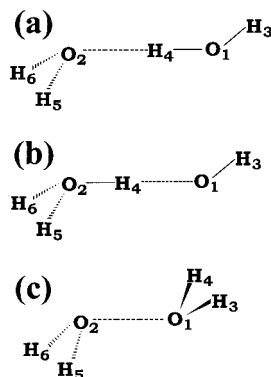*J. Phys. Chem. A, Vol. 106, No. 16, 2002* **4201**



**Figure 1.** Structures of water dimer: (a) neutral; (b) proton-transferred cation; (c) hemibonded cation.

the ionization of water dimer. At the MP4 level of theory, hemibonded $(H_2O-H_2O)^+$ isomer has been found[43] to lie 8.9 kcal/mol above the proton-transferred isomer. The results obtained with the modified coupled pair functional (MCPF) method provided[44] a similar result. There are some discrepancies in the prediction[45,46] of the minimum energy isomer of this system if one considers the recent density functional calculations with gradient-corrected exchange correlation functionals (like BP86, BLYP, B3LYP etc), which predict the hemibonded isomer as the global minimum structure. However, a density functional calculation with 50% exact Hartree−Fock exchange (in the BHLYP functional) does not show this discrepancy and provides[47] a better aggrement with the MP2 calculations, predicting the $(OH-H_3O)^+$ proton-transferred isomer to be the ground state. Recently, Sodupe et al.[47] ascribed this discrepancy to the overestimation of the exchange correlation functional due to the well-known self-interaction error in widely used density functionals. In view of the success of the present density functionals for many systems including loosely bound transition states, it is rather surprising that this discrepancy exists between the post-Hartree−Fock methods and density functional results (for most of the functionals) in determining the ground-state structure of this system. Thus, it would be interesting to study the multiconfiguration effect on the structures of different isomers and energetics for this open-shell radical system. In view of this, we have been motivated to apply a complete active space self-consistent field (CASSCF) theory to determine the ground-state isomer of water dimer radical cation and to calculate the accurate energy difference between the two isomers using a CASSCF wave function followed by multiconfigurational perturbation treatment, which has been successful for many complicated systems.[48] Moreover, the process of evolution of the geometry change of the water dimer on ionization, which involves an intramolecular proton transfer, is an interesting process to study through the profiles of hardness, polarizability, etc along the reaction coordinate. It may be noted that most of the earlier investigations[17−36] along these lines have dealt with geometry changes in conventional molecular systems rather than weak interaction as present in hydrogen-bonding systems as considered here.

Thus, the main objective of this work is twofold: first to obtain the equilibrium geometry of the two isomers (proton-transferred and hemibonded) using complete active space self-consistent field followed by total energy calculations using multiconfigurational quasi-degenerate perturbation theory and second to study the variations of chemical potential/electronegativity, hardness, and polarizability along the reaction coordinate for the proton-transfer process from the vertically ionized

water dimer radical cation $(H_2O)_2^+$ at the neutral hydrogen-bonded geometry to the proton-transferred structure (HO−$H_3O)^+$.

The plan of the paper is as follows: we discuss the computational method in section 2 and the results of numerical calculations in section 3. Finally, we present the concluding remarks in section 4.

## 2. Computational Methods

Ab initio molecular orbital methods have been used here to investigate the structures of the two most stable isomers of the $(H_2O)_2^+$ radical system. The stationary structures have been fully optimized with the CASSCF method in which the active space includes all of the valence electrons and all of the valence orbitals except the oxygen 2s orbitals. This results in an active space of 11 electrons and 10 orbitals and is referred to as CAS-(11/10). Single-point second-order multiconfigurational quasi-degenerate perturbation theory (MCQDPT2)[49] calculations have been carried out at the CAS(11,10) optimized geometries to improve the energies. The CASSCF and MCQDPT2 calculations in this work are performed using the GAMESS[50] electronic structure program using 6-31++G(d,p), 6-31++G(2d,p), and 6-31++G(2d,2p) basis sets. The polarizability is calculated using the coupled Hartree−Fock theory, and consequently, the other reactivity parameters considered here are also calculated with the Hartree−Fock method. For this purpose, the electronegativity (negative of the chemical potential, $\mu$) and hardness parameters denoting the first and second derivatives of energy as $\chi = -\mu = -(\partial E/\partial N)_v$ and $\eta = \frac{1}{2}(\partial^2 E/\partial N^2)_v$ are obtained within the finite difference approximation as

$$\chi = \frac{1}{2}[(E_{N-1} - E_N) + (E_N - E_{N+1})] \qquad (1)$$

$$\eta = \frac{1}{2}[(E_{N-1} - E_N) - (E_N - E_{N+1})] \qquad (2)$$

where $E_N$, $E_{N-1}$ and $E_{N+1}$ denote, respectively, energies of the atomic or molecular species and its positive and stable negative ions for the same geometry (at fixed external potential $v(\mathbf{r})$).

## 3. Results and Discussion

As already mentioned above, the two lower-energy stationary structures of $(H_2O)_2^+$ that can be obtained after the ionization of the water dimer are presented in Figure 1. The lowest electronic state for the three-electron hemibonded structure has been found to be $^2B_u$, while the same for the proton-transferred structure is the $^2A''$ state, which has already been observed by earlier workers. The O−O distances and the energy differences for the two structures calculated in the present work are reported in Table 1. It is also interesting to compare the energy difference, $\Delta E$ [$= E(\text{hemibonded}) - E(\text{proton-transferred})$] of the two isomers (20.8 and 1.9 kcal/mol at the CASSCF and CASSCF+MCQDPT2 level of theory, respectively) with the previous ab initio results. It is clear from the results that the proton-transferred structure is more stable as compared to the three electron hemibonded structure at both CASSCF and CASSCF+MCQDPT2 levels of theory. This is consistent with the previous results obtained using MP2 and CCSD(T) levels of theory[47] (5.2 and 6.6 kcal/mol at the MP2 and CCSD(T) level of calculations). However, it appears that the CASSCF method slightly overestimates the energy difference, whereas the CASSCF+MCQDPT2 energy differences are very close to the MP2 and CCSD(T) predicted values. This may be due to the

**TABLE 1: Calculated O−O Distances and Relative Energies for the Two Isomers of $(H_2O)_2^+$ with Different Basis Sets**

| method | basis set | proton-transferred $R_{O-O}$, Å | hemibonded $R_{O-O}$, Å | $\Delta E^b$, kcal/mol |
|---|---|---|---|---|
| CASSCF | 6-31++G(d,p) | 2.567 | 2.023 | 21.2 |
| CASSCF+MCQDPT2$^a$ | 6-31++G(d,p) | | | 3.2 |
| CASSCF | 6-31++G(2d,p) | 2.567 | 2.025 | 20.5 |
| CASSCF+MCQDPT2$^a$ | 6-31++G(2d,p) | | | 1.4 |
| CASSCF | 6-31++G(2d,2p) | 2.568 | 2.027 | 20.8 |
| CASSCF+MCQDPT2$^a$ | 6-31++G(2d,2p) | | | 1.9 |

$^a$ MCQDPT2 energies are calculated at the corresponding CASSCF geometries. $^b$ The energy difference $\Delta E = E$(hemibonded structure) − $E$(proton-transferred structure), where $E$ denotes the total energy.

absence of dynamic electron correlation effect in the CASSCF methodology. Thus, it is clear that the effect of electron correlation is stronger in the hemibonded structure in comparison to the proton-transferred structure and that is why the energy difference is reduced drastically in going from CASSCF to CASSCF+MCQDPT2 results. It is interesting to compare the geometrical parameters obtained earlier by using MP2 methods with the present values obtained using CASSCF method. For the proton-transferrred structure, the CASSCF/6-31++G(2d,-2p) calculated O−O distance (2.568 Å) is slightly higher than the corresponding MP2/aug-cc-pVDZ or CCSD(T)/aug-cc-pVDZ values (2.528 and 2.538 Å, respectively).[47] Table 1 also shows that the computed O−O distance for the hemibonded isomer remains almost the same with an increase in the number of polarization functions and the present values of the O−O distance are slightly smaller in comparison to the earlier MP2 or CCSD(T) values (2.039 and 2.048 Å respectively).[47] The calculated values of the hardness parameter are found to be 7.6 and 5.8 eV for the proton-transferred and hemibonded structures, respectively. It is of interest to note that the energetically lower proton-transferred structure is associated with a higher value of hardness parameter in consistency with the principle of maximum hardness.

It is thus observed that the hydrogen atom involved in hydrogen bonding in a neutral water dimer gets transferred as a proton from one water molecule to the other on ionization of the dimer. Here, we investigate this proton-transfer process through the study of profiles of several reactivity parameters in addition to the energy variation. We start with the oxygen−oxygen distance ($R_{O-O} = 2.988$ Å) corresponding to the geometry of the neutral dimer and consider vertical ionization leading to the formation of the radical cation with the same geometry. We then follow the minimum energy path for the proton transfer at this fixed oxygen−oxygen distance. For this purpose, the hydrogen-bonded hydrogen atom has been moved gradually from the electron-acceptor water molecule toward the electron-donor water molecule to get the proton-transferred structure, and at each point. constrained geometry optimizations have been carried out at a fixed O−O and O−H distance ($O_1$−$H_4$ distance in Figure 1, considered here as the reaction coordinate) to get the minimum energy path. At those optimized geometries, different reactivity parameters have been calculated as outlined above and their profiles along the reaction coordinate have been obtained. The calculation has been repeated for several values of the O−O distance.

The variations of the energy, polarizability, hardness, and chemical potential in going from the initial state (hydrogen-bonded structure) to the final state (proton-transferred structure) are shown in Figure 2 for the initial value (2.988 Å) of O−O distance. It is observed that the process is associated with an
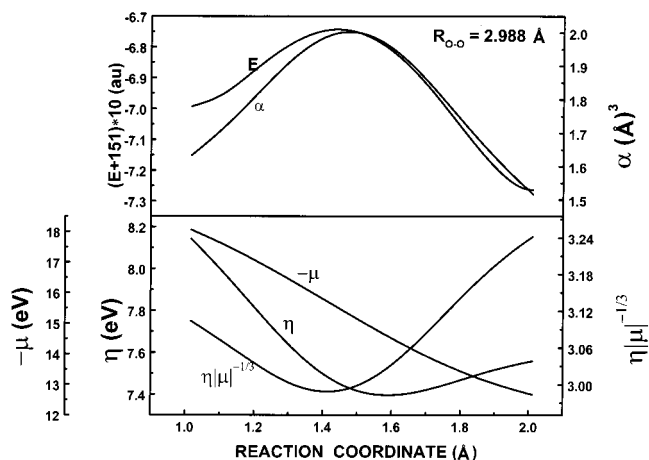


**Figure 2.** Variations of total energy ($E$), polarizability ($\alpha$), chemical potential ($\mu$), hardness ($\eta$), and *scaled hardness* ($\eta/|\mu|^{1/3}$) along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen−oxygen distance of 2.988 Å.

activation energy and the polarizability profile passes through a maximum corresponding to the transition state. The hardness profile also passes through a minimum, but the position of the corresponding O−H distance is slightly shifted from the transition state. Thus, the principle of minimum polarizability corresponding to lower energy is satisfied quite well, and the maximum hardness principle is also satisfied, although the minimum hardness does not correspond to the state of highest energy, that is, the transition state, exactly. It is in fact known that the principle of maximum hardness is actually associated strictly with a process of constant chemical potential. In this particular case, as shown in the plot, the chemical potential undergoes drastic variation; in fact, the extent of variation of chemical potential is much more than the hardness variation. We therefore are tempted to plot hardness scaled with inverse chemical potential, and it is observed that the plot of the *scaled hardness* ($\eta/|\mu|^{1/3}$) shows a minimum exactly corresponding to the geometry of the transition state. Because this process of proton transfer at this O−O distance is associated with an activation energy, the probability of proton transfer is less at this O−O distance although the final energy is lower. Thus, we reduce the O−O distance in steps and study the profiles of these parameters for the proton-transfer process at each value of O−O distance. Thus, in Figures 3−6, we show the energy variation for the proton-transfer process at the $R_{O-O}$ values equal to 2.88, 2.78, 2.68, and 2.581 Å. The energy barrier slowly reduces with decrease of $R_{O-O}$, and finally at $R_{O-O} = 2.581$ Å, it almost disappears making the proton transfer a barrierless process. The polarizability, hardness, and *scaled hardness* profiles show similar trends in all of these cases. The activation energies for the proton transfer at all of these O−O distances are shown in Table 2. In the spirit of earlier work on activation hardness,[51] we have also included the values of the "activation hardness" and the "activation polarizability" in the same table. It is interesting to note that as the activation energy decreases the activation hardness and activation polarizability also show a decrease.

The picture that emerges is that as the O−O distance slowly reduces from $R_{O-O} = 2.988$ Å to $R_{O-O} = 2.581$ Å there is a gradual elongation of the O−H bond simultaneously. This is quite obvious because the H atom being lighter is expected to adiabatically follow the minimum energy configuration as the O−O distance is varied. Finally at $R_{O-O} \approx 2.581$ Å, the proton gets transferred to its new configuration corresponding to the equilibrium geometry of the ionized state dimer.
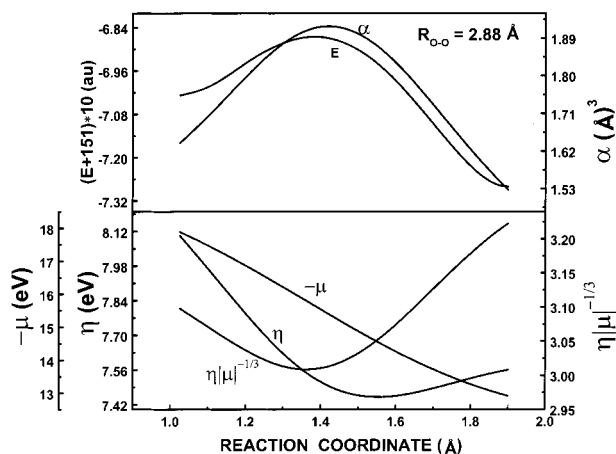
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**Figure 3.** Variations of total energy ($E$), polarizability ($\alpha$), chemical potential ($\mu$), hardness ($\eta$), and *scaled hardness* ($\eta/|\mu|^{1/3}$) along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen–oxygen distance of 2.880 Å.
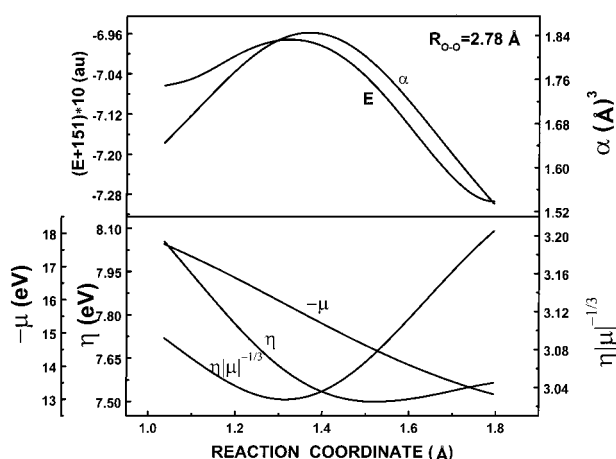


**Figure 4.** Variations of total energy ($E$), polarizability ($\alpha$), chemical potential ($\mu$), hardness ($\eta$), and *scaled hardness* ($\eta/|\mu|^{1/3}$) along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen–oxygen distance of 2.780 Å.
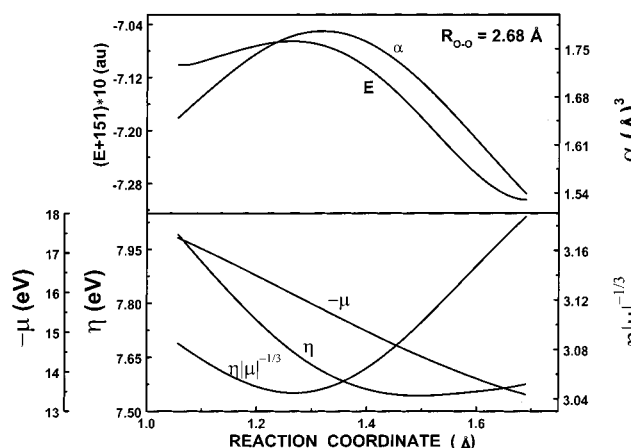


**Figure 5.** Variations of total energy ($E$), polarizability ($\alpha$), chemical potential ($\mu$), hardness ($\eta$), and *scaled hardness* ($\eta/|\mu|^{1/3}$) along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen–oxygen distance of 2.680 Å.

## 4. Concluding Remarks

The study of variation in energy and other reactivity parameters of molecules as a function of intramolecular rearrangement of the constituent atoms provides interesting insight
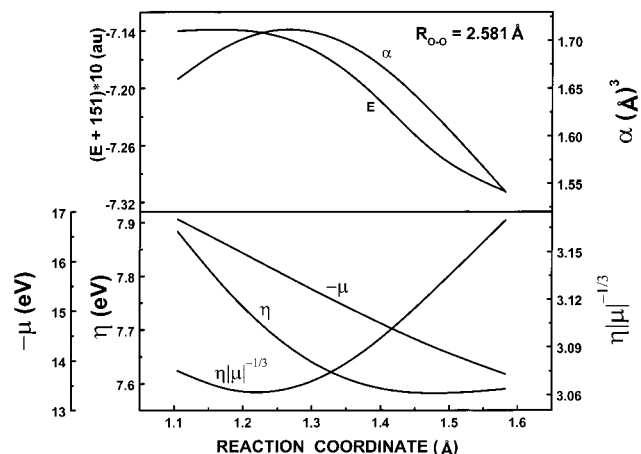


**Figure 6.** Variations of total energy ($E$), polarizability ($\alpha$), chemical potential ($\mu$), hardness ($\eta$), and *scaled hardness* ($\eta/|\mu|^{1/3}$) along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen–oxygen distance of 2.581 Å.

**TABLE 2: Calculated Values of the Activation Energy ($\Delta E^{\#}$), Activation Hardness ($\Delta\eta^{\#}$), and Activation Polarizability ($\Delta\alpha^{\#}$) for the Proton-Transfer Process at Different O–O Distances**

| $R_{O-O}$ (Å) | $\Delta E^{\#}$ (kcal/mol) | $\Delta\eta^{\#}$ (eV) | $\Delta\alpha^{\#}$ (Å³) |
|---|---|---|---|
| 2.988 | 15.7 | 0.686 | 0.366 |
| 2.880 | 10.2 | 0.574 | 0.275 |
| 2.780 | 5.8 | 0.458 | 0.195 |
| 2.680 | 2.2 | 0.320 | 0.119 |
| 2.581 | 0.1 | 0.106 | 0.034 |

into the various atom-transfer processes in chemistry. The present work has been concerned with an ab initio theoretical investigation of the proton-transfer process in water dimer on ionization. It is shown that in comparison to the cation radical at the neutral dimer geometry (corresponding to the vertical ionization), the energetically stable proton-transferred structure is associated with higher *scaled hardness* and lower polarizability as well. Analogously, it is also shown that the energetically most stable proton-transferred structure of the cation radical is associated with maximum hardness. To obtain insight into the process of proton transfer, the profiles of energy, hardness, polarizability, chemical potential, and *scaled hardness* have been calculated theoretically. The activation energy for the proton-transfer process is shown to have direct correlation with the polarizability and hardness parameters. Also, the study of these profiles further strengthens the principles of maximum hardness and minimum polarizability as applied to the weakly interacting hydrogen-bonded system studied here. Further work on the applicability of the concept of *scaled hardness* to other systems is in progress.

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