A quantitative and a qualitative study of the resonance assisted double proton transfer in formic acid dimer

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Ab initio molecular dynamics simulations have been performed to study the nature of the synchronous double proton transfer in formic acid dimer. In order to understand the evolution of the bonding during the double proton transfer, the electron localization function and the molecular orbital isosurfaces have been used. During the dynamics of the double proton transfer in formic acid dimer the two formic acid monomers approach each other, forming Speakman-Hadzi type of short strong hydrogen bonds at the transition state. The Speakman-Hadzi type of short strong hydrogen bonds are also shown to be polar covalent bonds. Based on the concept of resonance assisted hydrogen bond proposed by Gilli et al. (Gilli P, Bertolasi V, Ferretti V & G. Gilli, J Am Chem Soc, 116 (1994) 9093), it is shown that the proton at the transition state is connected by a pi-conjugated O—C=O structures, indicating a resonance assisted hydrogen bond. On this basis the double proton transfer process in the formic acid dimer can be termed as a resonance assisted double proton transfer. The present work indicates that the synchronous double proton transfer in the formic acid dimer is due to the formation of (a) Speakman-Hadzi type of short strong hydrogen bonds, and (b) resonance assisted hydrogen bond at the transition state.

For the past several years inter and intra-molecular proton transfer (PT) in hydrogen bonded systems has been recognized as one of the most fundamental and important phenomena in chemical and biological sciences and PT has received considerable attention, both from theoretical and experimental point of view. Single proton transfer (SPT) has been extensively studied in the last few decades, where malonaldehyde has been the prototypical molecule, particularly for the study of intra-molecular SPT. Multiple proton transfer (MPT), which involves more than one PT, plays a crucial role in bio-chemical and organic processes. Double proton transfer (DPT) is one of the model examples of MPT which involves the transfer of protons either synchronously or asynchronously in intermolecular hydrogen bonded systems. Tautomeric proton transfer in the hydrogen bonded base pair of DNA and proton relay systems in many enzymatic reactions are typical examples in biological systems.

Interestingly, recent studies have shown that the excited state dynamics of PT gives rise to significant quantum mechanical effects, such as tunneling. In a recent study, tunneling was shown to play a significant role in the PT even at room temperature. Recently, Ushiyama and Takatsuka have studied the time dependent probability of quantum tunneling in tropolene using a quasisemiclassical approach. It has also been shown that the solvent effects in the PT reactions can change the nature of PT.

It has been shown that during PT there is formation of short, strong hydrogen bonds (SSHB) or low barrier hydrogen bonds (LBHB) which play important role in stabilizing the transition state in many enzymatic reactions. Frey et al. found evidence of LBHB in the catalytic triad of a serine protease between aspartate and histidinium.

Kim et al. recently showed that the SSHB involved in the formamide-formic acid dimer is of Coulomb type where the H atom is more localized, rather than a Speakman-Hadzi type in which the H atom is delocalized between the two homonuclear atoms. Interestingly, in the last decade Gilli et al. used the crystal structure correlation method to categorize the SSHB into resonance assisted hydrogen bonding (RAHB) and charge assisted hydrogen bonding (CAHB). They showed that in RAHB the H atom is attached to the two oxygen atoms through pi-conjugated double bonds. Recently, ab initio path
integral techniques have been implemented to study the proton transfer properties of the charged water complexes where the strength of the hydrogen bond has been discussed at room temperature.\(^5\) Hence, it is of interest to understand how the SHSB’s are formed during the PT reaction and how they affect the PT process.

It is worth mentioning that during the transfer of proton from one atom to another, the surrounding atoms should adjust to new equilibrium positions. These environmental effects due to the PT processes are accompanied by a significant reorganization in the charge distribution.\(^20\) This electronic rearrangement during PT may lead to spectral changes that can be very important in photochromic molecules.\(^3\) Although the PT reactions involve change in the equilibrium positions of the surrounding nuclei, thus affecting the electronic charge distribution, there has been little discussion on the change in the nature of bonding during the PT. Recently, Krokidis et al.\(^21\) used electron localization function (ELF) and catastrophe theory to discuss the change in the bonding pattern of C=C and C—C=O pi conjugation during the SPT in malonaldehyde and showed that these heavy atoms have a non-vanishing effect on the PT rate. In a very recent work Chochiouisová et al.\(^22\) explained the red-shifted O---H---O and improper blue shifted C---H----O hydrogen bonds of the first local minimum of the formic acid dimer (FAD) using natural bond orbital analysis and rehybridization. Interestingly they showed that the red shifted O---H----O is due to the hyperconjugation and improper blue shifted C---H----O has a mesomeric structure which is due to the delocalization of electron density from C---H \(\sigma^*\) ‘antibonding orbital’\(^22\).

In the present study, we have chosen the formic acid dimer as a model system to study the evolution of bonding during the DPT. To study the bonding analysis, we have used ELF and molecular orbital pictures in combination with the ab initio molecular dynamics (AIMD) simulation in a canonical (constant temperature) ensemble.

FAD is considered to be a strong hydrogen bonded (O---O < 2.7 Å) system.\(^23\) Activation barrier and the structural properties of FAD have been well studied\(^\text{23-27}\). Due to the low mass of protons it has been argued whether the DPT process in FAD is a quantum tunneling or a classical effect\(^\text{28a,23-27}\). Madeja and Havenith\(^24\) in a recent experimental work first used fully analyzed high resolution spectrum to show that the tunneling splitting of the DPT in DCOOH dimer is 0.00286 cm\(^{-1}\), corresponding to a proton transfer time of 5.8 ns. In this study, the energy barrier was shown to be 12.1 kcal/mol. Madeja et al.\(^28\) have also identified polar isomers of formic acid dimers in helium droplets. Kim\(^\text{23}\) used variational transition state theory (VTST) for multidimensional semiclassical tunneling approximations to show that tunneling is effective in FAD.\(^\text{23}\) He calculated the barrier height as 8.94 kcal/mol at a G2* level. Chang et al.\(^\text{28a}\) obtained a tunneling splitting of 0.3 cm\(^{-1}\) (proton transfer time ~ 55 ps), while Shida et al.\(^\text{28b}\) used a 3D potential energy surface and obtained a barrier height of 12.0 kcal/mol and a tunneling splitting of 0.004 cm\(^{-1}\). Vener et al.\(^25\) used the same approach as Shida et al.\(^\text{28b}\) but with more accurate ab initio calculations showed the tunneling splitting to be 0.3 cm\(^{-1}\). In a very recent work, Tautermann et al.\(^27\) used the VTST including the quantum chemical effects like tunneling to calculate the reaction rates and the transmission coefficients in the temperature range of 100 – 400 K and for various isotopic substitutions. Ito and Nakanaga\(^\text{29}\) have shown that the spectral pattern for (HCOOH)\(_2\) and (DCOOH)\(_2\) isomers are different from each other. Subsequently, Florio et al.\(^30\) showed that the O—H and the C—H stretch of local modes of FAD mix while forming the normal modes. In an interesting experiment, Howard and Kjærgaard\(^31\) used an intracavity laser photoacoustic spectroscopy to study the vibrational analysis of the formic acid isotopomers HCOOH and DCOOH. They observed that the O—H stretching vibration in HCOOH and DCOOH is quite different. In another spectroscopic experiment, Matyútsik et al.\(^32\) for the first time found the rotational constants of the regular O—H----O/ O---H----O isomer of (HCOOH). From the above spectroscopic study, it is clear that the O—H frequency in (DCOOH)\(_2\) and (HCOOH)\(_2\) are different. Hence, it is questionable to compare the results of the DPT in (DCOOH)\(_2\) and (HCOOH)\(_2\).

Several studies on FAD have confirmed that there is a synchronous DPT in the gas phase FAD\(^\text{23-27,31-35}\). In an important work, Miura et al.\(^34\) have applied the AIMD technique to study the synchronous DPT in FAD for a period ~5 ps. Ushiyama et al.\(^35\) also used the same approach as Miura et al.\(^\text{34}\), but found the proton transfer time to be 150 fs, which is very low as compared to the earlier studies. Wolf et al.\(^\text{23}\) performed molecular dynamics using a projected
augmented wave method to study the simultaneous proton transfer in FAD\textsuperscript{35}. They carried out the dynamics for a period of 20 ps at a temperature of 500-700 K. However, asynchronous DPT was shown to take place in the presence of the solvent by Kohanoff et al.\textsuperscript{36}.

Based on this earlier background, we revisited the dynamics and the structural investigation of DPT in FAD by using the AIMD simulation in a canonical ensemble (constant temperature). Further, we have focused our investigation on understanding the change in the bonding of FAD during the DPT. We have used ELF and molecular orbital isosurfaces to investigate the evolution of bonding during the DPT process in FAD. Becke and Edgecombe\textsuperscript{37,38} proposed the concept of ELF which is one of the important tools to understand the nature of bonding in many chemical systems. ELF has been used to elucidate sigma, pi, polar covalent, ionic bonds and the delocalization in the aromatic systems and in metallic bonding\textsuperscript{38,39}. ELF also accounts for the change in the bonding during a chemical reaction\textsuperscript{39}.

**Theoretical Methods and Computational Details**

All the calculations presented in this paper have been performed using the VASP code\textsuperscript{40}. The AIMD technique used in VASP\textsuperscript{41} treats the nuclear motion classically and simultaneously evaluates the instantaneous electronic ground state using the Kohn-Sham equations within the generalized gradient approximation (GGA) with the Perdew-Wang 91 (PW-91) functional\textsuperscript{42}. We have used GGA instead of local density approximation (LDA), since GGA has been shown to give an accurate description of hydrogen bonds\textsuperscript{43}. The present method uses the plane wave basis set in conjunction with the ultra-soft pseudopotentials\textsuperscript{44}. Miura et al.\textsuperscript{34} have already shown that the results obtained for the DPT in FAD from the localized basis set and the plane waves are same. The dimer was placed in an orthorhombic supercell of dimension $a=13.19\,\text{Å}$, $b=4.00\,\text{Å}$, $c=11.59\,\text{Å}$. The equations of motion were integrated with a time step of 0.5 fs. The forces on the atoms after each dynamic step were converged to -0.001 eV/Å. Earlier theoretical studies have reported the study of the DPT in FAD in the range 100 - 400 K\textsuperscript{23,25,33,34}. In the present study, we have kept the temperature of the FAD system at 200±40 K using Nose-Hoover thermostat\textsuperscript{45}. The total simulation was carried out for a period of 25 ps. Initially, the FAD system was thermally equilibrated for a period of 2.5 ps, where we observed large fluctuation in the temperature. A constrained dynamics was also performed to understand the effect of the motion of the heavy atoms.

The nature of bonding was studied using ELF. There are several reviews, which discuss the technical details and applications of ELF in a broader perspective. Here, we give only a brief discussion on ELF. In the present study, ELF was calculated as follows:

\[
ELF = \frac{1}{1 + \left(\frac{D}{D_h}\right)^2}
\]

\[
D_h = \frac{3}{10} (3\pi^2)^{2/3} \rho^{4/3}
\]

\[
D = \frac{1}{2} \sum_i \left| \nabla \phi_i \right|^2 - \frac{1}{8} \frac{\left| \nabla \rho \right|^2}{\rho}
\]

where $\phi_i$ are the Kohn-Sham orbitals, $D$ is the excess local kinetic energy due to Pauli repulsion obtained from the difference between the definite positive kinetic energy density of actual fermionic system and that of the von Weiszacker kinetic energy functional and $D_h$ is the Thomas-Fermi kinetic energy. It has been shown that the ELF values lie between 0 and 1 (ref. 37). The excess kinetic energy takes low values in regions occupied by the paired electrons and this leads to the values of the ELF close to unity showing a localized domain, while low values of ELF reflect a delocalized region as in metallic systems\textsuperscript{38}. It is, therefore possible to define regions of space that are associated with different electron pairs in a molecular system. The present ELF calculations are based on the valence electrons, while the core electrons are replaced by the ultra-soft pseudopotential.

**Results and Discussion**

We present the structural and dynamical aspects of the DPT and in the latter part of the discussion, we present a critical analysis of the evolution of the bonding during the DPT in FAD.

**Structure and dynamics**

The structural parameters for the equilibrium and the transition state structures of FAD are given in
The DPT process in FAD is schematically described in Scheme 1. Structures 1 and 3 in Scheme 1 describe the two equilibrium structures, while Structure 2 represents the transition state structure on the potential energy surface.

Bond length distribution of the covalent bond (r1) and the electrostatic hydrogen bond (r2) for the total simulation period from 5 ps to 25 ps (equilibration period is not included) is given in Fig. 1, where r1, r2, r3 and r4 are the internal coordinates defined in Scheme 1. For \(~-16\) ps the O---H (r1) and the O--H (r2) bonds fluctuate in their mean positions and no PT is observed (Fig. 1). Around 18.8 ps, the r1 bond lengthens and the r2 bond shortens. At \(~-18.8\) ps, both the bonds cross each other and the r1 bond is converted into r2 and vice versa (shown by an arrow), hence indicating a PT. In the same manner, the other proton in FAD also simultaneously moves from one monomer to another, when r3 changes to r4 and vice versa and has a similar behavior as shown in Fig. 1. This reveals that there is a DPT taking place in FAD at \(~18.8\) ps. This confirms the earlier theoretical investigations where the DPT in FAD was shown to take place in the ps range.23-27, 33-35. It is noteworthy to mention that if the slopes of the graphs in Fig. 2 or Fig. 3 deviate from the value 1, the proton motion during the OPT becomes asynchronous. Thus, the slopes of the plots shown in Scheme 1.

Earlier studies have successfully analyzed the synchronous nature of DPT in FAD.23,33-35. Before we proceed to the analysis of O--C--O structure, it is necessary to give a brief discussion on the synchronous DPT process in FAD. From now onwards we present the data between 17 ps and 20 ps where the evolution of the DPT process takes place as shown in Scheme 1. To illustrate the simultaneous motion of both the protons in FAD, we plotted the change in the bond length distribution of the covalent O---H bonds (r1 versus r3) (Fig. 2) and the electrostatic O--H hydrogen bonds (r2 versus r4) (Fig. 3). The linear regression of the graphs in Figs 2 and 3 has the same slope of 0.98, implying that the change in the bond length of covalent O---H bonds (r1 and r3) and the hydrogen O--H bonds (r2 and r4) is symmetric. This shows that the motion of both the protons from one monomer to the other is synchronous, which agrees with the earlier results.23-27, 33-35.

### Scheme 1

#### Table 1—Structural parameters of the equilibrium and the transition state structures obtained from ab initio molecular dynamics simulations using Parr-Wang 91 (PW-91) functional have been compared with the experimental, and the density functional using Becke Lee Yang Parr exchange correlation functional. Bond lengths are given in Å, bond angles in degrees.

<table>
<thead>
<tr>
<th></th>
<th>Expt.</th>
<th>Equilibrium structure</th>
<th>Transition state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AIMP (PW-91)</td>
<td>B-LYP</td>
</tr>
<tr>
<td>d(O--O)</td>
<td>2.703</td>
<td>2.611</td>
<td>2.645</td>
</tr>
<tr>
<td>d(H--O)</td>
<td>1.667</td>
<td>1.570</td>
<td>1.626</td>
</tr>
<tr>
<td>d(O--H)</td>
<td>1.036</td>
<td>1.033</td>
<td>1.019</td>
</tr>
<tr>
<td>d(C--O)</td>
<td>1.323</td>
<td>1.308</td>
<td>1.322</td>
</tr>
<tr>
<td>d(C--H)</td>
<td>1.220</td>
<td>1.238</td>
<td>1.233</td>
</tr>
<tr>
<td>|O--H--O</td>
<td>1.082</td>
<td>1.102</td>
<td>1.098</td>
</tr>
<tr>
<td>|H--O=C</td>
<td>180.0</td>
<td>178.8</td>
<td>179.9</td>
</tr>
<tr>
<td>|C--O--H</td>
<td>125.3</td>
<td>120.4</td>
<td>122.5</td>
</tr>
<tr>
<td>|C--H=C</td>
<td>108.2</td>
<td>112.0</td>
<td>110.6</td>
</tr>
<tr>
<td>|O=C--O</td>
<td>126.2</td>
<td>126.6</td>
<td>126.4</td>
</tr>
<tr>
<td>|H=C--O</td>
<td>115.4</td>
<td>120.7</td>
<td>121.7</td>
</tr>
</tbody>
</table>

*Ref. 48

*Ref. 30
Fig. 1—The bond length fluctuation of covalent bond O—H (r1) (shown by black line) and hydrogen bond O—H (r2) (shown by the red line) for a period of 25 ps at \( T = 200 \pm 40 \) K. The arrow indicates the conversion of r1 to r2 and vice-versa.

in Fig. 2 and Fig. 3 together decide the degree of synchronization of the DPT process.

Moreover, it has been shown that the DPT process in FAD is initiated by a concerted inter-monomer vibration, which brings both the monomer units close to each other.\(^8\)\(^,\)\(^16\) This allows the O—O distance to reduce and favors a synchronous PT. On this basis we studied the dynamics of the O—O distance which indicates the inter-monomer change and correlates it with the O—H and O—O bond length fluctuations. To discuss this issue we define two parameters:

\[
\rho_1 = (r_2-r_1) + (r_4-r_3),
\]

\[
\rho_2 = r_1+r_2+r_3+r_4
\]

\( \rho_1 \) indicates the O—H and O—O bond length fluctuations and the change in \( \rho_2 \) indicates the inter-monomer fluctuations during the DPT between 17 and 20 ps.

Fig. 2—Bond length fluctuation of the covalent O—H bonds of the formic acid dimer r1 and r3 in the range of 17—20 ps. The linear regression is shown by a straight line.

Fig. 3—Bond length fluctuation of the hydrogen bonds in the formic acid dimer r2 and r4 in the range of 17—20 ps. The linear regression is shown by a straight line.
The plot of $\rho_1$ versus $\rho_2$ is given in Fig. 4. Interestingly, we see that the quadratic regression of the graph of $\rho_1$ versus $\rho_2$ (Fig. 4) is a parabola. The plot in Fig. 4 agrees very well with the earlier results by Miura et al.\(^{34}\) Kim et al. showed that the intermonomer vibration during the DPT in the formamidine-formic acid dimer had a similar behavior as in Fig. 4, however the nature of DPT was shown to be asynchronous.\(^{16}\) The positive and the negative values of $\rho_1$ in Fig. 4 indicate the fluctuations in the O—H and O—O—H bonds of FAD before and after the DPT, respectively. The structure of FAD at $\rho_1=0$ (where $r_1=r_2=r_3=r_4$) is the transition state (Scheme 1 (Str 2)) which is observed at $\sim 18.8$ ps. The barrier height for the DPT, which is $6.6$ kcal/mol is given in Table 2.

We can also see from Table 2 that the DPT barrier calculated by us using PW-91/plane wave and the other higher level theoretical calculations match within $\pm 1.2$ kcal/mol. It should be noted that the barrier for the DPT in FAD obtained in the present investigation and by most of the earlier theoretical calculations disagree with the experimental results for the DPT in DCOOH dimer (Table 2). Moreover, the time scale for the DPT in DCOOH was shown to be in nano-second\(^{28}\) which does not match with some of the earlier theoretical results\(^{33-35}\). The reason for this would either be the deuterium effect in DCOOH dimer as discussed earlier or the higher tunneling splitting of the DPT in DCOOH dimer or may be both\(^{28}\). It is out of scope to discuss this issue in the present investigation. However, we have focused on the change in the bonding structure during the DPT in FAD.

The minimum of the parabola (Fig. 4) confirms that the transition state has the shortest inter-monomer distance, where the O—O—O distance is 2.468 Å (Table 1). At the transition state ($\rho_1=0$), the H atom lies between the oxygen atoms. This allows the H atom to get delocalized between the two oxygen atoms, hence forming a Speakman-Hadzi type of SSHB\(^{14,17}\). The shortening of the intermonomer distance and the formation of Speakman–Hadzi type of SSHB stabilizes the transition state and the barrier is lowered. This lowering of the transition state barrier due to the formation of SSHB may allow the protons to cross the barrier classically rather than by a quantum tunneling. The formation of SSHB also makes the H atoms form polar covalent bonds with the oxygen atoms on either side, which is discussed in the next section. In the initial phase of the simulation we observed an asynchronous motion of the protons which may be due to larger intermonomer distance resulting in weak hydrogen bonds. It is evident from the above discussion that the DPT takes place when the intermonomer distance is at minimum and results in the formation of Speakman-Hadzi type of SSHB.

**Table 2—The barrier height of the double proton transfer in formic acid dimer calculated by Parr-Wang-91 (PW-91) presented in this work is compared with other theoretical calculations**

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>Barrier height (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>12.10</td>
<td>24</td>
</tr>
<tr>
<td>PW-91/Plane wave</td>
<td>6.60</td>
<td>Present work</td>
</tr>
<tr>
<td>B-LYP/Plane wave</td>
<td>5.40</td>
<td>30</td>
</tr>
<tr>
<td>B3-LYP/6-31G(d,p)</td>
<td>5.40</td>
<td>47</td>
</tr>
<tr>
<td>B3-LYP/6-311G(2d,2p)</td>
<td>6.40</td>
<td>49</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ</td>
<td>7.89</td>
<td>27</td>
</tr>
<tr>
<td>G2</td>
<td>8.94</td>
<td>23</td>
</tr>
<tr>
<td>MP2/aug-cc-pVTZ</td>
<td>6.71</td>
<td>27</td>
</tr>
</tbody>
</table>

*The experimental barrier given is for (DCOOH)$_2$.\(^{2}$*
Ushiyama et al.\textsuperscript{35} showed that the deformation in the O--C--O structure in FAD plays a vital role during the DPT. Towards this, we focus our study on the bond length fluctuations of C=O and C--O. Gilli et al.\textsuperscript{18,19} have used $\lambda$ parameter to analyze the RAHB in many hydrogen bonded systems. In the present work, we have generalized the $\lambda$ parameter to discuss the resonance in the O--C--O structures. We define two $\lambda$ parameters corresponding to the two O--C--O structures in FAD,

$$\lambda_1 = \left(1 + Q_1/Q^0\right)/2.0$$

$$\lambda_2 = \left(1 + Q_2/Q^0\right)/2.0$$

where $Q_1 = r_6-r_5$ and $Q_2=r_7-r_8$, where $r_5$, $r_6$, $r_7$ and $r_8$ are as shown in Scheme 1 (Str 1), and $Q^0$ is the same quantity for the pure single (C--O) and double bond (C=O) which remains constant. In our study, $Q^0 = 0.07$. When $Q_1 = Q_2=0$ the bonds between C and O atoms are equal and $\lambda_1 = \lambda_2 = 0.5$, which indicates a resonance within O--C--O structures. We plotted $\lambda_1$, $\lambda_2$ as a function of time between 17-20 ps which corresponds to the DPT process in Fig. 5. In Fig. 5 before the DPT, $\lambda_1 = 1$ and $\lambda_2 = 0$ indicate the bond length fluctuations of C--O and C=O of the Str 1 in Scheme 1. At $\lambda_1 = \lambda_2 = 0.5$, the horizontal line cuts the graph (shown by an arrow in Fig. 5) and indicates the resonance in the O--C--O structures. It was also observed that the horizontal line cuts the graph at $\approx 18.8$ ps where the transition state was located (Fig. 4). $\lambda_1 = 0$ and $\lambda_2 = 1$ indicates the bond length fluctuations of C--O and C=O of the Str 3 in Scheme 1. Hence, the above observation reveals that there is resonance in both the O--C--O structures of FAD during the DPT.

Next, we established the correlation of the resonance in the O--C--O structures and the dynamics of the synchronous DPT. For this we plotted $\rho_1$ versus $\rho_3$ (Fig. 6), where $\rho_1$ is as defined earlier and $\rho_3 = (r_8-r_7) + (r_6-r_5)$. $\rho_1$ is the fluctuation in all the four O and H bonds, while on the other hand, $\rho_3$ shows the dynamical change of the C and O bonds. When $\rho_3=0$, all the bonds between C and O

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Plot of the coupling parameter $\lambda_1$ (black line), $\lambda_2$ (red line) as a function of time between 17 ps and 20 ps. The arrow indicates $\lambda_1=\lambda_2=0.5$ showing a resonance in both the O--C--O structures of the formic acid dimer.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{Plot of the distribution function of $\rho_3$ as a function of $\rho_1$ in the range of 17 - 20 ps of the formic acid dimer.}
\end{figure}
will have the same bond lengths and will indicate a resonance in the O—C—O structure. The correlation coefficient of the linear regression of this graph is 0.94. This shows that there is a simultaneous evolution of the resonance in the O—C—O structures and the synchronous motion of the DPT. We also observed that the linear regression passes through \( \rho_1 = \rho_3 = 0 \), indicating that the resonance in the O—C—O structures occurs at the transition state. This reveals that the H atoms at the transition state, which are Speakman-Hadzi type of SSHB, are attached to the oxygen atoms on either side by a \( \pi \)-conjugated double bond and can be termed as RAHB. Hence, our finding on the structural and dynamical data of DPT in FAD clearly demonstrates that the formation of Speakman-Hadzi type of SSHB and the RAHB leads to synchronous DPT in FAD. Hence, the DPT in FAD is a resonance assisted DPT.

In order to investigate the role of heavy atoms, we have also carried out a constrained dynamics simulation by fixing all the atoms except the hydrogen atoms involved in the hydrogen bonding. We found that the hydrogen atoms only wiggle at the same position and no proton transfer was observed. It can be seen that for the proton transfer to take place, it is necessary to relax all the degrees of freedom in the system.

**Bonding**

In the present section, we discuss the bonding evolution during the DPT in FAD with the help of ELF at different isosurface values and the molecular orbital at one third of the maximum isosurface value.

Figure 7 describes the ELF isosurfaces of the ground state (left column), isomer (right column) and the transition state (middle column) of FAD at different isosurface values. Figure 8 describes the molecular orbital isosurfaces of the ground state structures (left and right) and the transition state structures.

![Fig. 7](image_url)

Fig. 7—Left column: 3D representation of the ELF of the ground state structure of Scheme 1 (Str 1) at different isovales. The black spheres are the C atoms, the white spheres indicate the H atoms and the grey spheres represent the O atoms. [(a) ELF=0.78, (b) ELF=0.82 (c) ELF=0.84]. The regions I and II represent the C=O and the C—O, respectively, region III represents the O—H bond, region IV represents the hydrogen bond between the H of one monomer with the O atom of the other, region V shows the lone pair of electrons on the oxygen atom of C=O. Middle column: 3D representation of the ELF of the transition state structure shown in Scheme 1(Str 3). [(d) ELF=0.78; (e) ELF=0.82; (f) ELF=0.84]. The ELF distribution shows a symmetric distribution. Regions I and II indicate the resonance in the O—C—O structure. Region IV indicates the polar covalent bond between the O and H atoms. Right column: 3D representation of the ELF of the isomer structure of Scheme 1 (str 3) at different isovales. [(g) ELF=0.78; (h) ELF=0.82; (i) ELF=0.84]. The ELF isosurfaces of the isomer are the mirror images of the ground state structure (left column).

![Fig. 8](image_url)

Fig. 8—The 3D isosurfaces of the highest occupied molecular orbital (HOMO) at one third of the maximum isovalue of the (a) ground state, (b) transition state and (c) isomer. The black spheres are the C atoms, the white spheres indicate the H atoms and the grey spheres represent the O atoms. The isosurfaces of the HOMO of the (a) ground state and (b) the isomer show the \( \pi \) orbital on the O atoms of the C=O. The isosurface of HOMO of the transition state (c) shows the \( \pi \)-orbital on all the oxygen atoms.
(middle) at one third of its maximum isovalue. Five different localization regions have been recognized as shown in Fig. 7, which change during the proton transfer in FAD. One-third isosurface values are useful because it makes the bonding easy to visualize and predict the densities.

ELF = 0.78 isovalue (Fig. 7a) of the ground state FAD shows that there is a circular electron localization, indicated by region I which describes a double bond between the C and O atoms. Regions II and III show sigma bond between C—O and O—H respectively. No localization region is seen in region IV. This is due to the existence of the hydrogen bond between the oxygen of one monomer of FAD with the hydrogen of the other. Region V represents the lone pair of electrons of the oxygen atoms. At a higher isosurface value of ELF = 0.82 (Fig. 7b), all the localization regions are completely separated and clearly indicate double bond, single bond and the lone pair of electrons. Even at a higher ELF isovalue of 0.84 (Fig. 7c) we see localization in the regions III and V, which implies that the lone pairs and the covalent O—H bonds are highly localized. Figure 8 shows the isosurface of the highest occupied molecular orbital (HOMO) which shows a pi-orbital of the O of the C=O. The isovalue for the ELF were chosen beyond 0.75 because of the covalent bonding, which reflects the strong localization of electrons in the system.

However, the ELF isosurfaces of the transition states are strikingly different from those of the ground state. ELF at 0.78 (Fig. 7d) of the transition state shows a symmetric electron localization isosurface. The localization in the regions I and II are same on both the monomers of FAD. This indicates that all the C—O bonds are same. Moreover, the region V also shows an identical localization domain on all the oxygen atoms. At ELF = 0.8 (Fig. 7e), we clearly see that all the four C—O bonds have similar localization. This reveals that there is a resonance in the O—C—O region of both the monomers. This is in agreement with the earlier discussion on structure and dynamics where we observed that at the transition state all the four C—O bonds are equal. However, we also see a localization domain in the region IV which was seen to be empty in the ground state (Fig. 7a).

Surprisingly, we did not observe any localization region on the H atoms involved in the hydrogen bonds indicating H+ ions. Region V that was shown to be a lone pair of electrons in the ground state (Fig. 7a) had been deformed and the localization region was polarized towards the H+ ions. On increasing the ELF value from 0.8 to 0.84 isovalue (Fig. 7f) we observed a symmetric localization region between the O—H and H—O bonds. This is due to the protons lying in the mid-way of O—H—O, which has been discussed in the earlier section. Interestingly, this arrangement of the H+ lying in the center of the oxygen atoms and polarizing the electron density over the oxygen atoms allows it to form an intermediate electrostatic-covalent bond with the oxygen atoms on either side (Fig. 7f), which is often called as a polar covalent bond.

This kind of polar covalent bond has been seen in some enzymes when the H lies in the middle of the two oxygen atoms. The formation of polar covalent bonds at the transition state can be attributed to the formation of Speakman-Hadzi type of SSBH. The isosurface of HOMO (Fig. 8b) of the transition state shows a pi orbital on all the oxygen atoms, which is in contrast with the HOMO of the ground state (Fig. 8a) where the pi orbitals were seen only on the carbonyl oxygen atoms.

In Fig. 7, the right column shows the ELF isosurfaces of the isomer of the ground state of FAD after both the proton transfers take place from one monomer to the other through the transition state. From Fig. 7 we clearly see that the ELF isosurfaces of the ground state FAD (left column) and its isomer (right column) are mirror images of each other. The regions I, II, III of the ground state (Fig. 7) have been changed to II, I, IV of the isomer (Fig. 7g) respectively. The HOMO isodensity (Fig. 8c) shows pi orbitals on the oxygen atoms of C=O as expected.

The above study shows that ELF along with the HOMO isosurfaces play a significant role in understanding the evolution of the bonding structure during the DPT in FAD.

Conclusions
We have performed AIMD simulations for a period of 25 ps at 200±40 K in combination with a qualitative analysis of the ELF and molecular orbital analysis to investigate the nature of the synchronous proton transfer of DPT in FAD. Our investigation shows that the synchronous motion of the protons during the DPT in FAD is due to the two important factors, viz., (1) heavy atom (oxygen atoms) displacement, which allows the formic acid monomers to approach each other and causes the H atoms to delocalize between the oxygen atoms,
forming a Speakman-Hadzi type of SSHB, which is also a polar covalent bond, and (2) resonance in both the O—C—O structures of FAD allows the H atom to form RAHB. Hence, on account of the RAHB, the DPT in FAD can be termed as resonance assisted double proton transfer. Our study suggests that if the H atom is involved in RAHB and a Speakman-Hadzi form RAHB. Hence, on account of the RAHB, the forming a Speakman-Hadzi type of DPT is a classical effect or a quantum tunneling. Further theoretical investigations are necessary to understand if the discrepancies between the theory and experiments are due to the deuterium effect or any fundamental lacuna in the conventional molecular dynamics calculations used. The present theoretical investigation however, should suffice to understand the bonding structure during the PT reactions, which would be otherwise difficult to understand through experimental methods. The present work would also help in understanding the role of SSHB and RAHB during the PT reactions in biological systems such as DNA base pairs and enzymatic reactions.

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