Pseudo Jahn-Teller Origin of the Double Proton Transfer Energy Barrier in Formic Acid Dimer

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Introduction
Proton transfer is one of the simplest and most fundamental reactions in chemistry and biology. Multiple proton transfer is also ubiquitous in living organisms, such as in DNA mutation reactions or enzyme catalysis reactions. In this field, double proton transfer systems are of tremendous importance because they can serve as a template for DNA base pairs. Carboxylic acid dimers are often used as models for multiple proton transfer, of which formic acid dimer (FAD) is the simplest. Therefore, the FAD system has long been considered as a prototype for several proton transfer studies [1-3]. Of course, it should be noted that a real simulation of the proton transfer process in the real chemical or biological environment would require a more complex model, because such factors as solvent molecules, water molecules (hydration sphere), local electric field, etc., play important roles. In this work, the double proton transfer in the formic acid dimer was studied quantitatively chemically by the Pseudo Jahn-Teller Effect (PJTE) approach.

Results and discussion
The results of ab initio calculations of the adiabatic potential energy surfaces for the double-proton transfer in the FAD are rationalized in terms of the pseudo Jahn-Teller effect (PJTE) [4-6].

The planar nuclear configuration of D₂h symmetry of this dimer corresponds to the transition state (TS) for the transfer of two central hydrogen atoms at equal distance between the two molecules of the formic acid (see Table 1). In this configuration, the system has the singlet ground electronic state 1⁠A₀ and imaginary frequency 1770.38 cm⁻¹ which corresponds to displacement of b₁g-type (Fig. 1a). This means the D₂h configuration of the FAD is unstable with respect to the symmetry-adapted distortion b₁g of two central hydrogen atoms (Fig. 1b). It is due to the relatively strong vibronic coupling of the ground state 1⁠A₀ with the low-lying excited state 1⁠B₁g resulting in the two-levels PJTE (A₀+B₁g)@b₁g problem.

Table 1. Optimized geometric and electronic parameter for FAD in the TS (D₂h) and deformed (C₃v) configurations.

<table>
<thead>
<tr>
<th></th>
<th>D₂h</th>
<th>C₃v</th>
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<tbody>
<tr>
<td>¹Eₜ</td>
<td>-377.6361 u.a.e.</td>
<td>-377.6647 u.a.e.</td>
</tr>
<tr>
<td>¹α₀ (b₀)</td>
<td>1770.38 cm⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>¹Rₛ₋₀</td>
<td>1.186 Å</td>
<td>0.959 Å</td>
</tr>
<tr>
<td>¹R₀₋₀</td>
<td>2.373 Å</td>
<td>2.803 Å</td>
</tr>
<tr>
<td>∠OCO</td>
<td>126.3 °</td>
<td>125.9 °</td>
</tr>
<tr>
<td>²q (H⁺)</td>
<td>0.386</td>
<td>0.322</td>
</tr>
<tr>
<td>²q (O)</td>
<td>-0.475</td>
<td>-0.373</td>
</tr>
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</table>

The PJTE parameters (see Table 2) were evaluated by fitting the ab initio calculated adiabatic potential energy curves to the analytic expression for the energy obtained in the theory of the PJTE:

\[ e_{1,2} = \frac{1}{4}(K_{1g} + K_{2g}Q^2 + \Delta + \frac{1}{2}\sqrt{\left[ K_{1g} - K_{2g}\right]^2 - 4F^2Q^2}) \]

Calculated PJTE parameters:

K₁g = 19.43 eV/Å²
K₂g = 405.14 eV/Å²
F = 17.08 eV/Å
Δ = 14.31 eV
K₀ₐ = K₀₁ - 2F²/Δ = -21.36 eV/Å².

Conclusions
In this work, using the formic acid dimer system as an example, it was demonstrated that hydrogen bonds in carboxylic acid dimers can be described within the Pseudo Jahn-Teller Effect; all the potential energy curves calculated along the displacements of the central protons towards one of the monomer-molecule coincide entirely with those predicted by the general vibronic theory. Thus, the functional dependence of the potential energy on the instability coordinates of Q₁g resulting from the PJTE theory, with the parameters estimated by quantum-chemical calculations, can serve as a pre-parametrized analytic model of the adiabatic potential, which can be used to simulate the double proton transfer in such systems.

References: