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. plays important roles. In this work, the double proton transfer in the formic acid dimer was studied quantitatively chemically by the Pseudo Jahn-Teller Effect (PEJT) 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 D_{2h} 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 ^1A_g and imaginary frequency 1770.38 cm^{-1} which correspondes to displacement of b_{1g} -type (Fig. 1a). This means the D_{2h} configuration of the FAD is unstable with respect to the symmetry-adapted distortion b_{1g} of two central hydrogen atoms (Fig. 1b). It is due to the relatively strong vibronic coupling of the ground state ^1A_g with the low-lying excited state $^1B_{1g}$ resulting in the two-levels PJTE $(A_g+B_{1g})\otimes b_{1g}$ problem.

Table 1. Optimized geometric and electronic parameter for FAD in the TS (D_{2h}) and deformed (C_{2h}) configurations.

	D_{2h}	C_{2h}
E_{tot}	-377,6361 u.a.e.	-377.6647 u.a.e.
ω_i (b_{1g})	1770,38 cm^{-1}	-
R_{H^*-O}	1.186 Å	0.959 Å
R_{O-O}	2.373 Å	2.803 Å
$\angle$ OCO	126.3 °	125.9 °
q (H*)	0.386	0.322
q (O)	-0.475	-0.373

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:

$$\varepsilon_{1,2} = \frac{1}{4}(K_{01}+K_{02})Q^2 + \frac{\Delta}{2} \mp \frac{1}{2}\sqrt{\left[\frac{1}{2}(K_{01}-K_{02})Q^2 - \Delta\right]^2 + 4F^2Q^2}$$

Calculated PJTE parameters:
$K_{01} = 19.43$ eV/Å^2
$K_{02} = 405.14$ eV/Å^2
$F = 17.08$ eV/Å
$\Delta = 14.31$ eV
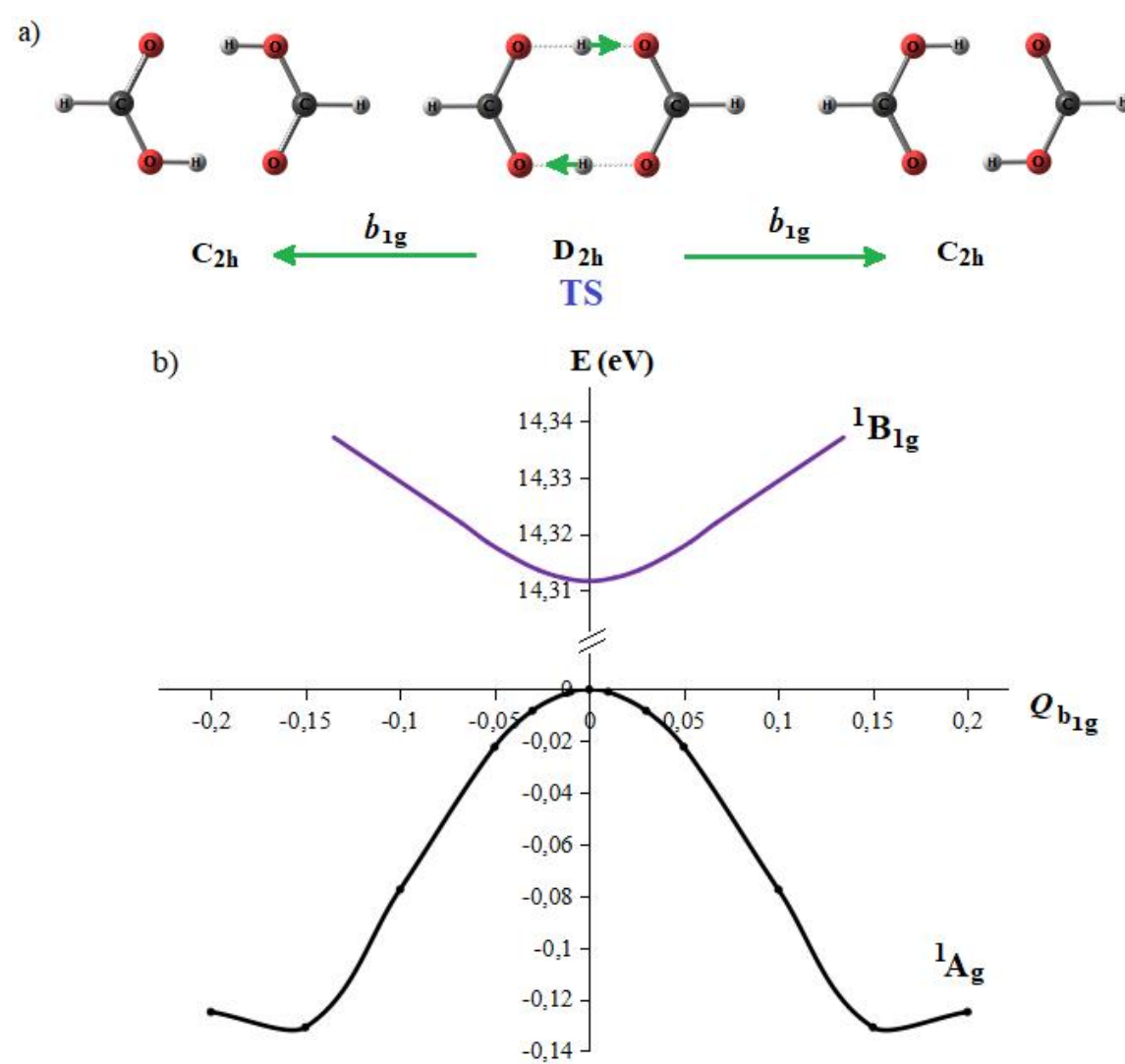$K_{gr} = K_{01} - 2F^2/\Delta = -21.36$ eV/Å^2.

Fig. 1. (a) Reaction coordinate (b_{1g}) in FAD; (b) cross-sections of the APESes for the ground ^1A_g and the excited $^1B_{1g}$ states of FAD along the b_{1g} distortion

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 $\varepsilon(Q_{b_{1g}})$ resulting from the PEJT theory, with the parameters estimated by quantum-chemical calculations, can serve as a pre-parametrized analytical model of the adiabatic potential, which can be used to simulate the double proton transfer in such systems.

References:
1) LIU, H.; CAO, J.; BIAN, W. *Double proton transfer in the dimer of formic acid: an efficient quantum mechanical scheme.* Front. Chem., 2019, 7(676), pp. 1-10. DOI: 10.3389/fchem.2019.00676
2) FARFÁN, P.; ECHEVERRI, A.; DIAZ,E.; TAPIA, J.D.; GÓMEZ, S.; RESTREPO, A. *Dimers of formic acid: Structures, stability, and double proton transfer.* The Journal of Chemical Physics, 2017, 147, 044312, pp. 1-8. DOI: 10.1063/1.4985880
3) CAMINATI, W.; LI, W.; EVANGELISTI, L.; GOU, Q.; MEYER, M. *Barrier to proton transfer in the dimer of formic acid: a pure rotational study.* Angew. Chem. Int. Ed., 2019, 131(3), pp. 869-875. DOI: http://dx.doi.org/10.1002/ange.201812754
4) BERSUKER, I.B.; *Chemical Reviews*, **121**, 1463–1512 (2021).
5) GORINCHOY, N.; BALAN, I.; POLINGER, V.; BERSUKER, I. *Pseudo Jahn-Teller origin of the proton-transfer energy barrier in the hydrogen-bonded [FHF]- system.* Chemistry Journal of Moldova, 2021, 16(1), pp. 115-120. DOI: http://dx.doi.org/10.19261/cjm.2021.834
6) GERU, I.I.; GORINCHOY, N.N.; BALAN, I.I. *Pseudo Jahn-Teller origin of the proton tunneling in Zundel cation containing water clusters.* Ukranian Journal of Physics, 2012, 57(11), pp. 1149-1155. http://nbuv.gov.ua/UJRN/Ukjourph_2012_57_11_9