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

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The results of *ab initio* calculations of the adiabatic potential energy surfaces for the double-proton transfer in the formic acid dimer (FA_2) are rationalized in terms of the pseudo Jahn-Teller effect (PJTE).

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 dimer. In this configuration, the system is in a singlet ground electronic state ^1A_g with imaginary frequency of 1770.38 cm^{-1} of the b_{1g} mode (Fig. 1a). This means the D_{2h} configuration of the dimer FA_2 is Jahn-Teller unstable with respect to the symmetry-adapted displacement b_{1g} of the central hydrogen atoms (Fig. 1b). It is due to the relatively strong vibronic coupling of the ground-state ^1A_g term to the low-lying excited term $^1B_{1g}$ to the symmetry-breaking b_{1g} mode resulting in the PJTE $(A_g+B_{1g})\otimes b_{1g}$.

(a)	(b)	**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
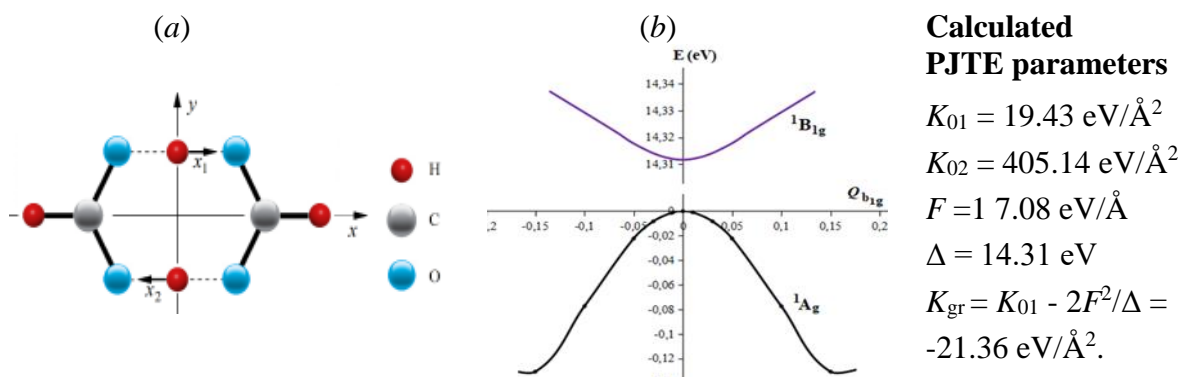$K_{gr} = K_{01} - 2F^2/\Delta = -21.36$ eV/Å^2.

Fig. 1. (a) Reaction coordinate (b_{1g}) in formic acid dimer; (b) cross-sections of the APESes for the ground ^1A_g and excited $^1B_{1g}$ states of FA_2 along the b_{1g} distortion

The PJTE parameters 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 [1]:

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

[1] Isaac B. Bersuker; *Chemical Reviews*, **121**, 1463–1512 (2021).