

The Jahn–Teller and pseudo-Jahn–Teller effects in the propyne radical cation

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The Jahn-Teller (JT) and pseudo-Jahn-Teller (PJT) effects [1] in propyne radical cation is studied theoretically [2]. A vibronic coupling model [3] is constructed in a diabatic electronic basis using symmetry rules and normal coordinates of the electronic ground state of propyne. Extensive *ab initio* electronic structure calculations are carried out to construct the potential energy surfaces of first three low-lying \tilde{X}^2E , \tilde{A}^2E and \tilde{B}^2A_1 electronic states of propyne radical cation. It is found that the JT effect is weak in the \tilde{X}^2E state as compared to that in the \tilde{A}^2E state. Because of large energy separation, the PJT coupling among the JT-split components of the \tilde{X}^2E state with the neighboring states is also very weak. However, the PJT coupling of the \tilde{B}^2A_1 state with the JT split components of the \tilde{A}^2E state has some impact on the dynamics in the coupled \tilde{A}^2E - \tilde{B}^2A_1 electronic states. The nuclear dynamics calculations are carried out from first principles by both time-independent and time-dependent quantum mechanical methods. The vibronic spectrum is calculated and assigned and the results are compared with the experiment [4]. The nonradiative internal conversion dynamics of excited states is examined. Interesting comparison is made with the JT and PJT coupling effects in the nuclear dynamics of the \tilde{X}^2E - \tilde{A}^2E - \tilde{B}^2B_2 electronic states of the isomeric allene radical cation [5].

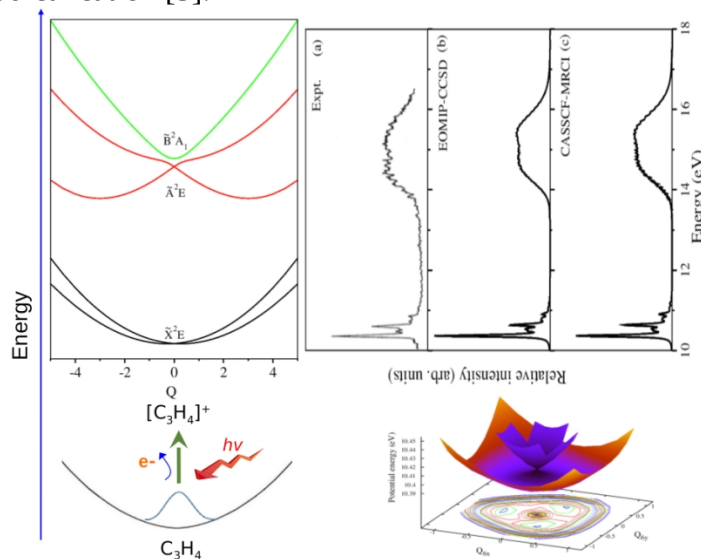


Figure: Schematic potential energy surfaces and coupled vibronic band spectrum.

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