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 \textit{ab initio} electronic structure calculations are carried out to construct the potential energy surfaces of first three low-lying \(X^2\)E, \(\tilde{A}^2\)E and \(\tilde{B}^2\)A\(_1\) electronic states of propyne radical cation. It is found that the JT effect is weak in the \(X^2\)E state as compared to that in the \(\tilde{A}^2\)E state. Because of large energy separation, the PJT coupling among the JT-split components of the \(X^2\)E state with the neighboring states is also very weak. However, the PJT coupling of the \(\tilde{B}^2\)A\(_1\) state with the JT split components of the \(\tilde{A}^2\)E state has some impact on the dynamics in the coupled \(\tilde{A}^2\)E-\(\tilde{B}^2\)A\(_1\) 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 \(X^2\)E-\(\tilde{A}^2\)E-\(\tilde{B}^2\)B\(_2\) electronic states of the isomeric allene radical cation [5].

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