The Role of the Transition Density in the S0 - S1 and S0 - S2 Transitions of Fulvene with Next Generation QTAIM

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Abstract

We present, for the first time the S0 - S1 (S01) and S0 - S2 (S02) transition densities for fulvene, using the 3-D next generation QTAIM constructed using the preferred direction of electronic charge density accumulation. There is a symmetrization of the position of the bond critical point (BCP) of the torsional C2-C6 BCP along the bond-path associated with the presence of a conical intersection (CI) between the ground and first excited state (S1). The corresponding transition density S0 - S1 (S01) displays hindered BCP motion that is associated with a large rearrangement of the total electronic charge density, made apparent by the form of a 3-D bond-path. The reaction pathway for the second excited state does not have an associated CI to an adjacent state along this path, or symmetrization of the BCP position for the S0 - S2 (S02) transition density, or hindered motion, or a large deviation in the 3-D bond-path. We hypothesize that the symmetrization of the position of the torsional C2-C6 BCP along a bond-path for an excited state pathway is associated with a CI, where the transition density BCP is hindered and as a consequence the electron density undergoes a large rearrangement, made apparent by the form of the 3-D bond-path.

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