Quadratic to higher-order Jahn-Teller coupling effects and subfemtosecond proton dynamics in tetrahedral systems

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Neutral Methane and neopentane, and negatively charged alanate anion are having T_d equilibrium structure in ground state. Ionization of an electron from their highest occupied molecular orbitals yield CH_4^+ , $C(CH_3)_4^+$ and AlH_4 in their X^2T_2 state. According to Jahn-Teller (JT) theory both the cations and AlH_4 are unstable on this electronic manifold and expected to form new JT minima. Indeed, C_{2v} minimum energy structures are observed experimentally for CH_4^+ while it is of C_{3v} symmetry for $C(CH_3)_4^+$. However, AlH_4 is unstable to AlH_2+H_2 or AlH_3+H asymptotes with local minimum structures of D_{2d} and C_{2v} symmetry. In all three cases their first photoelectron bands are broad with highly irregular vibronic structures. Additionally, a recent measurement of the structural rearrangement of methane upon ionization using high-harmonic generation (HHG) technology, suggests such an event in CH_4^+ to be occur in subfemtosecond regime [1].

In this presentation, I shall discuss the origin of such distinct structural symmetry, underlying details of their photoelectron bands and the subfemtosecond proton dynamics of CH_4^+ via an *ab initio* quantum dynamics study [2-4]. A comparison of stabilization energies for T_2 x *e*-, T_2 x t_2- and T_2 x $(e+t_2)$-JT problems suggest that the structural evolution of $C(CH_3)_4^+$ from T_d to C_{3v} configurations is occur via JT active t_2 mode, whereas CH_4^+ rearranges to C_{2v} structure through a combination of JT active *e* and t_2 bending vibrations. A comparison of the ratio of squared autocorrelation functions of CD_4^+ and CH_4^+ in their ground states with the experimentally observed ratio of HHG signals of CH_4 and CD_4 suggests a local minimum structure of CH_4^+ to occur in ~1.85 fs. Additionally, the structural evolution is predicted to begin through activation of the a_1 and *e* modes which conducts the original T_d symmetry of the cation to a D_{2d} structure. At ~1.85 fs, the intermediate D_{2d} structure is further predicted to rearrange to local C_{2v} geometry via t_2 bending vibration. While CH_4^+ and $C(CH_3)_4^+$ are treated with quadratic JT coupling, the higher-order JT coupling effect is found to be important to correctly reproduce the first photoelectron band of AlH_4^-.

References

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