A full-dimensional quantum dynamics study is carried out for the highly fluxional H$_{2}^+$ cation on a recent reference potential energy surface [1] by using the multi configuration time-dependent Hartree-fock method. [2] With five equivalent light atoms and shallow barriers between various low-lying stationary points on the surface, the spectroscopic characterization of H$_{2}^+$ represents a huge challenge for accurate quantum dynamics simulations. The present calculation [3] is the first such a study on this cation, which together with its isotope analogues are of primary importance in the interstellar chemistry. The vibrational ground state properties and several vibrationally excited states corresponding to low vibrational frequency motions, not yet directly observable by the experiment, are presented and analyzed.

**Kinetic Energy Operator.**

The full-dimensional PESs Xie et al. [1] has been employed. The 9 degrees of freedom are combined into 5 modes $q$ according to the following scheme: $q_1 = \{z, R\}$, $q_2 = \{x, y, z\}$, $q_3 = \{\alpha, u_{\alpha}\}$, $q_4 = \{R_{2}\}$ and $q_5 = \{R_{1}\}$. An n-mode representation of the potential is used. The potential $V(q)$ is given by:

\[
V = \sum_{i,j}^{\beta} v^{(i\beta)}(q_i, q_j) + \sum_{i}^{\alpha} v^{(i\alpha)}(q_i, q_i) + \sum_{i,j,k}^{\delta} v^{(i\delta)}(q_i, q_j, q_k)
\]

with $v^{(i\beta)}$ being the potential at a reference geometry $a$ $(V(a))$ and the other terms come by:

\[
\begin{align*}

v^{(i\alpha)}(q_i, q_i) &= V(q_i, q_i, a^{(i\alpha)}) - V(q_i, a^{(i\alpha)}) - V(a^{(i\alpha)}, q_i) + V(a^{(i\alpha)}, a^{(i\alpha)})

v^{(i\delta)}(q_i, q_j, q_k) &= V(q_i, q_j, q_k, a^{(i\delta)}) - V(q_i, q_j, a^{(i\delta)}, q_k) - V(q_i, a^{(i\delta)}, q_j, q_k) - V(a^{(i\delta)}, q_i, q_j, q_k)

v^{(i\beta)}(q_i, q_j) &= V(q_i, q_j, a^{(i\beta)}) - V(q_i, q_j) - V(a^{(i\beta)}, q_i, q_j) + V(a^{(i\beta)}, a^{(i\beta)})

\end{align*}
\]

Here, $a^{(i\alpha)}$ represents the reference point $a$ except the $i$th coordinate and $a^{(i\beta)}$, $a^{(i\delta)}$ represent the reference point $a$ except the $(i, j)$ and $(i, j, k)$ coordinates, respectively. The POTFIT program is then used to convert the potential terms of the expansion in the sum of products of single-particle operators form required by the MCTDH program.[2]