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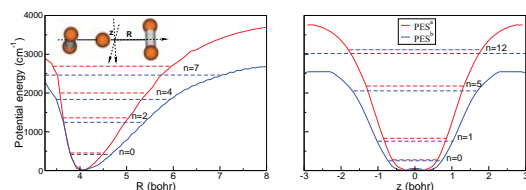
## Spectral simulations and vibrational dynamics of the fluxional $\text{H}_5^+$ cation and its isotopologues: signatures of the shared-proton motions

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**Synopsis** The recent increased interest on research studies of the  $\text{H}_5^+$  cation, and its isotopologues, is due to the postulation for their presence, although still not detected, in the interstellar medium. There is no doubt, particularly in the light of the recent laboratory observations, that the spectroscopy of these systems is also a great challenge for the theorists. Thus, we report the first fully converged coupled anharmonic quantum study on vibrational dynamics of these highly fluxional cations, providing important information on their spectroscopy in a rigorous manner, and open perspectives for further investigations.

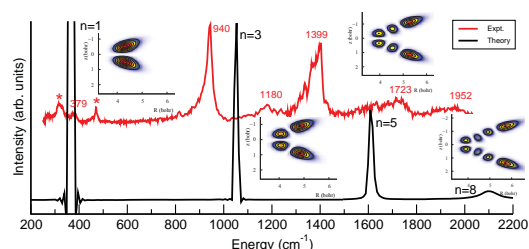
Full-dimensional (9D) multiconfiguration time-dependent Hartree (MCTDH) computations are reported for the vibrational states of the  $\text{H}_5^+$  and its deuterated isotopologues employing recent first-principles potential energy surfaces [1]. With five equivalent light atoms and shallow barriers between various low-lying stationary points on the surface (see figure 1), the spectroscopic characterization of  $\text{H}_5^+$  represents a huge challenge for accurate quantum dynamics simulations. It is found that these systems are highly delocalized, interconverting between equivalent minima through rotation and internal proton transfer motions even at their vibrational ground state. Isotopic substitution affects the zero-point energy and structure, showing preference in the arrangements of the H and D within the mixed clusters, and the most stable conformers of each isotopomer are the ones with the H in the central position. Several vibrationally excited states corresponding to low vibrational frequency motions (see figure 1), not yet all of them directly observable by the experiment, [2] are presented and analyzed.



**Figure 1.** Minimum energy path (solid lines) of the PESs along the R and z coordinates. The energy values (dashed lines) of the indicated  $n$  vibrational states of the  $\text{H}_5^+$  is also for each PES.

Further, reduced dimensional quantum dynamics calculations of the infrared spectrum of the  $\text{H}_5^+$  and  $\text{D}_5^+$  clusters are reported in both below and above dissociation threshold [3]. The 4D

simulations are performed using time-dependent and time-independent approaches within the MCTDH method. Propagation of the wavepackets includes an absorbing scheme to deal with vibrational dissociating states, while to assign the different spectral lines block improved relaxation computations are performed. The predominant features in the spectra are assigned to the excitations of the shared-proton stretch mode (see figure 2), while above dissociation the symmetric and antisymmetric stretching of the two  $\text{H}_2$  and the breathing mode of the  $\text{H}_3^+$  are also involved. The computed infrared absorption spectra for both cations are in very good agreement with the recent experimental measurements available from multiple- and single-photon photodissociation spectroscopy [4, 2].



**Figure 2.** Simulated 4D-MCTDH spectrum for the  $\text{H}_5^+$ , and its comparison with the experimental IR-MPD measurements [2]. The assignment of the bands is also shown.

### References

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