

# A first-principles study of the rovibrational states of $H_5^+$ and its isotopologues

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$H_n^+$  clusters have been thoroughly searched for and investigated in the lab and extensive quantum chemical computations also exist for some of them with smaller  $n$  values. The first-principles study of the structure and the dynamics of the smallest important member of the  $H_n^+$  clusters, the  $H_5^+$  molecular ion and its isotopologues, is a serious challenge as traditional techniques of quantum chemistry and molecular spectroscopy are not applicable, one needs to resort to fourth-age techniques of quantum chemistry.

To the best of our knowledge, despite the large number of recent quantum chemical investigations of the  $H_5^+$  molecular ion, only pure vibrational spectra were reported for the  $H_5^+$  molecular ion and its  $D_5^+$  isotopologue and even these only up to about  $1000\text{ cm}^{-1}$ . For the other isotopologues only the zero-point energies and perhaps a couple of excited states were determined and described. This shows the difficulties associated with a proper description of the rovibrational motion of these cations.

In this work, we report results of variational nuclear motion computations, utilizing the fourth-age code GENIUSH (*GE*neral rovibrational code with *N*umerical, *I*nternal-coordinate, *U*ser-Specified Hamiltonians) developed in our lab, concerning the rotational-vibrational energy levels of the  $H_5^+$  molecular ion and its isotopologues.

As GENIUSH allows this in a straightforward way, an attempt was made to describe rotations and vibrations of  $H_5^+$  *via* reduced-dimensional models, in which several internal coordinates were kept fixed at their equilibrium values. These computations provide approximate energy levels at a substantially reduced computational cost. In these models we thoroughly studied the interaction between the torsional vibration motion of the two  $H_2$  units of the cluster with respect to each other and the rotational motion of the molecular ion. When the results are compared to the rigid-rotor (RR) model, important deviations are found in the energy level structure which could be explained only using the RRD analysis of the rovibrational wave functions.

Furthermore, vibrational band origins (VBO) were determined both from reduced and full dimensional computations and they were compared to previous works. These results show that for some of the internal motions only full dimensional computations can yield dependable information, seemingly coupling of the several large-amplitude motions of the ion hinder the use of reduced-dimensional models even at the lowest excitations.

As to the possible deuterated isotopologues of  $H_5^+$ , attempts were made to study the existence of structural isomers. The results obtained do not seem to be completely convincing but suggest the existence of several isomers for the  $H_nD_{5-n}$ ,  $n = 1, 2, 3, 4$  cases.