THE TUNNELLING SPLITTINGS OF THE SOME STATIONARY VIBRATIONAL STATES OF THE HYDRONIUM ANION AND RADICAL DUE TO INVERSION MOTION

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Two closely related compounds, the $H_3O\cdot$ radical (HR) and H_3O^- anion (HA), are of significant interest in astrophysics. Both species exist as pyramidal isomers, but are not stable at room temperature. However, they can be stable at low temperatures and have been observed in interstellar space and comets. Similar to the ammonia molecule, HR and HA exist in two equivalent configurations, which makes tunneling between them possible. However, to our knowledge, no attempts have been made to calculate tunneling splittings even for the ground vibrational states of these species.

In this work, a non-standard set of vibrational coordinates was utilized to describe the inversion motion. The first coordinate used was the distance (h) between the oxygen atom and the plane formed by three hydrogen atoms. The second coordinate was a fully symmetrical coordinate q_{123}, which was composed of three coordinates (q_1, q_2, q_3) describing the distances between valence-free hydrogen atoms. These coordinates were tested on NH_3 and H_3O^+ species, and tunneling splittings of the ground states were obtained for both at the CCSD(T)/Aug-cc-pVQZ level of theory, yielding values of 0.78 and 53.5 cm^{-1}, respectively.

For the HR and HA species, calculations of the two-dimensional potential energy surface (2D PES) were performed at the UHF CCSD(T)/d-aug-cc-pVQZ, UHF CCSD(T)/aug-cc-pVQZ, and CCSD(T)/aug-cc-pVQZ, CCSD(T)/d-aug-cc-pVQZ levels of theory. The calculated tunneling splittings in the ground states of the hydronium anion (4.1 cm^{-1}) and radical (3.4 cm^{-1}) were found to be significantly lower than the tunneling splitting in the ground state of the hydronium cation (53.5 cm^{-1}).