

Molecular dynamics simulations of vibrational infrared and Raman spectra of H_5O_2^+

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Abstract

We report infrared (IR) and Raman vibrational spectra of H_5O_2^+ protonated water dimer using computational chemistry methods, the normal mode analysis (NMA) and molecular dynamics (MD) simulations. Various computational methods and basis sets were used. We also located the H_5O_2^+ stationary points on the potential energy surface using the Gaussian 16 program. The H_5O_2^+ Zundel complex serves as a benchmark system to study the proton transfer process. We also investigated IR and Raman intensities of other deuterated analogs, such as D_5O_2^+ , D_4HO_2^+ , and $\text{H}_4\text{D}^+\text{O}_2$.

Proton transfer frequencies estimated using the NMA method at the MP2/aug-cc-pVTZ level of theory for H_5O_2^+ , D_5O_2^+ , D_4HO_2^+ and $\text{H}_4\text{D}^+\text{O}_2$ were 911.3 cm^{-1} , 660.2 cm^{-1} , 831.2 cm^{-1} , and 719.6 cm^{-1} , respectively. Corresponding CCSD(T)/aug-cc-pVTZ values using the analytical potential energy surface were 861 cm^{-1} , 627 cm^{-1} , 786 cm^{-1} , and 692 cm^{-1} . Proton motion in H_5O_2^+ yields high IR activities, while OH-stretch vibrations show strong Raman activities. Currently we are running MD simulations at 100 K and 300 K to obtain IR and Raman spectra. This computational work will provide the baseline information to assess the anharmonic effects in the vibrational spectra.