First-principle molecular dynamics study of selected Schiff and Mannich bases: application of two-dimensional potential of mean force to systems with strong intramolecular hydrogen bonds.

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Rok wydania

2008

Czasopismo

Journal of Chemical Theory and Computation

Numer woluminu

4

Strony

375-384

DOI

10.1021/ct7002644

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Car-Parrinello Molecular Dynamics simulations were performed for selected anharmonic systems, i.e., Schiff and Mannich base-type compounds, to investigate the vibrational properties associated with 0-H stretching. Ail calculations were performed in the gas phase to compare them with available experimental data. First the vibrational properties of the two compounds were analyzed on the basis of well-established approaches: Fourier transformation of the autocorrelation function of both the atomic velocities and dipole moments. Then path integral molecular dynamics simulations were performed to demonstrate the influence of quantum effects on the proton's position in the hydrogen bridge. In addition, quantum effects were incorporated a posteriori into calculations of 0-H stretching envelopes for the Schiff and Mannich bases. Proton potential snapshots were extracted from the ab initio molecular dynamics trajectory. Vibrational Schrodinger equations (one- and two-dimensional) were solved numerically for the snapshots, and the 0-H stretching envelopes were calculated as a superposition of the 0→1 transitions. Subsequently, one- and two-dimensional potentials of mean force (1D and 2D pmf) were calculated for the proton stretching mode from the proton vibrational eigenfunctions and eigenvalues incorporating statistical sampling and nuclear quantum effects. The results show that the applied methodologies are in good agreement with experimental infrared spectra. Additionally, it is demonstrated that the 2D pmf method could be applied in systems with strong anharmonicity to describe the properties of the 0-H stretching mode more accurately. Future applications of the 2D pmf technique include, in principle, large biomolecular systems treated within the QM/MM framework.