

1B1a Molecular Structures in ground and excited vibrational states from quasi-classical direct ab initio MD

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[Introduction]

The recent progresses of computer power and electronic structure theory have enabled us to search for bottoms of potential energy surface with high accuracy. Molecular structures in real systems, however, distribute over all the possible coordinate spaces in certain vibrational states and observed structures are their mean structures. Furthermore, the definitions of observed structures are different depending on the methods of experiments. Therefore, theoretical methods are expected to be able to calculate the differently defined structures in vibrational states including excited states. In this study, we calculate the mean structures, r_0 , r_z and r_g , for OH and OD radicals and H₂O in ground or excited vibrational states according to the respective definitions.

[Calculation and Result]

To calculate the structures, we use (a) quasi-classical direct ab initio molecular dynamics (MD) [1] for OH and OD radicals and H₂O and (b) Fourier Grid Hamiltonian method (FGH) only for the radicals. The methods, (a) and (b), give classical and quantum mechanical mean structures, respectively. Using (a), trajectories of molecular vibration with certain quantum vibrational energies and amplitudes along their normal modes are obtained, in which potential energies and forces are calculated based on ab initio MO (MP2/aug-cc-pVTZ). Taking time averages of the classical trajectories from (a) gives classically averaged structures. Using (b), wave functions of vibrational states are obtained and averaged structures with the obtained wave functions give quantum mechanical averaged structures.

The results are shown in the right. The calculated structures compared well with the experimentally derived values. No difference is found between the classical and quantum mechanical mean structures for any of the molecules calculated here.

[Reference]

- [1] T. Yamada, M. Aida, Chem. Phys. Lett. 752 (2008) 315. [2] J.P. Maillard, J. Chauville, A.W. Mantz, J. Mol. Spectrosc. 63 (1976) 120. [3] G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Krieger, Florida, 1991. [4] W.S. Benedict, N. Gailar, E.K. Plyler, J. Chem. Phys. 24(6) (1956) 1139. [5] K. Kuchitsu, L.S. Bartell, J. Chem. Phys. 36(9) (1962) 2460.

