1E2a

Fundamental frequency from quasi-classical direct ab initio MD: $(H_2O)_2$ and $(H_2O)_2H^+$

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[Introduction]

We have shown that fundamental frequencies of simple molecules such as H_2 and H_2O are obtained from quasi-classical direct ab initio MD considering correspondence between classical and quantum mechanical frequencies [1,2]. In this study, we extend our earlier studies to cluster systems, water dimer, $(H_2O)_2$ and protonated water dimer, $(H_2O)_2H^+$. For $(H_2O)_2$ we calculate four vibrational modes of OH stretching as shown in Figure 1. For $(H_2O)_2H^+$, we focus our attention on the vibration of internal proton parallel to the H-bond axis, which have been vigorously studied experimentally and theoretically.

[Method and Results]

Using quasi-classical direct ab initio MD, 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 with ab initio MO (MP2/aug-cc-pVDZ). We obtain fundamental frequencies from IR spectra, by means of Fourier transformation of dipole moment auto-correlation function.

Here we show the result of $(H_2O)_2$ in Table I. The theoretical values obtained from MD, normal mode analysis (NMA), second-order perturbation theory (2PT), and virtual configuration interaction-vibrational self-consistent field theory (VCI-VSCF), are shown in Table I with experimental values. The theoretical methods except NMA include anharmonicity of potential energy surface. The result of our method (MD) agrees well with the result from 2PT. The values obtained from VCI-VSCF are at least 82 cm^{-1} higher than 2PT in spite of the same quartic force field based on MP2/aug-cc-pVDZ used for 2PT and VCI-VSCF.

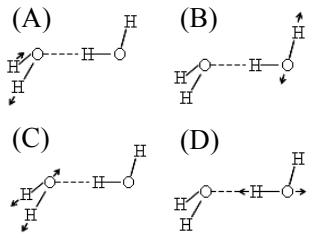

Figure 1

Table I (in cm^{-1})

	NMA	2PT	VCI-VSCF	MD	Expt.	
	MP2/aug-cc-pVDZ				Ref. [3]	Ref. [4]
(A)	3922	3731	3863	3728		3745.48
(B)	3904	3716	3828	3703	3735	3730
(C)	3798	3618	3744	3611		3600
(D)	3709	3556	3638	3553	3601	3530

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