1E3b   IR spectra of five-membered heterocycles by means of quasi-classical direct ab initio MD

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[Introduction]

The frequencies and the intensities of IR spectra are useful to get information concerning molecular conformation. It should be noted that the harmonic oscillator approximations is not always adequate for a molecule which has many conformational isomers with small energy barriers. Therefore, we adopt quasi-classical direct ab initio MD method in which the potential energy and forces are computed directly from ab initio MO method at each simulation step, to explore the conformational change and IR spectra.

[Calculation and Result]

We obtained local minimum structures and transition state structures for heterocycles with five-membered ring (cyclopentane, tetrahydrofuran, pyrrolidine), and normal vibrational analyses were done by means of ab initio MO method (MP2/6-31G*). Quasi-classical direct ab initio MD method (MP2/6-31G*) was applied with the condition of constant energy being equal to zero-point energy to get IR spectra. Program packages used for the calculations of ab initio MO and direct ab initio MD are Gaussiun03 and HONDO, respectively.

Two local minima (twist form; I, J) and one transition state structure (envelope form; TS) are shown in Fig 1. The local minima are in mirror image and interchangeable by the puckering motion; this conformational change is referred to as pseudorotation, because the positions of ring atoms undulate during the change. The energy barrier along pseudorotaion is small (1.35 kJ/mol). IR spectrum of tetrahydrofuran from MO method is shown in Fig 2. Spectrum (A) is based on the harmonic oscillator approximation for structure (I). Spectrum (B) shows the fundamental frequencies from direct ab initio MD method, which compares well with experimental spectra.
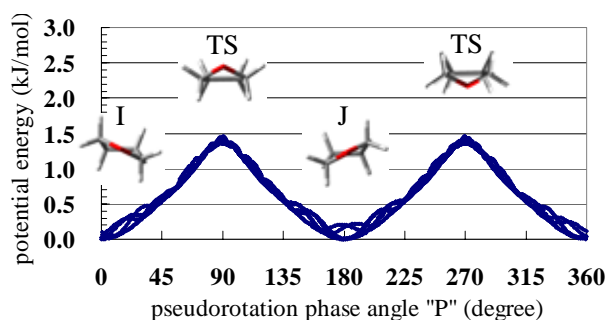

Figure 1. Pseudorotational pathway. I and J are the local minima and TS is the transition state. The energy difference between I (J) and TS is 1.35 kJ/mol.
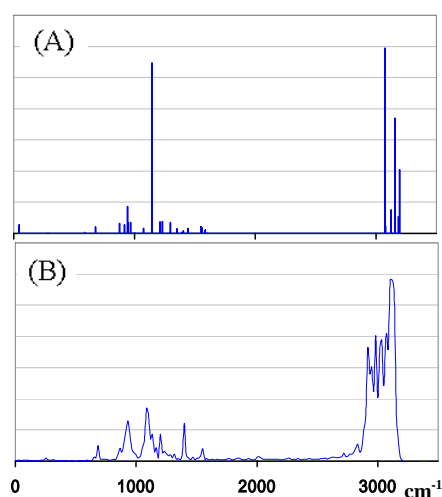

Figure 2. IR spectra of tetrahydrofuran. (A): Spectrum of structure (I) from harmonic oscillator approximation; (B): From quasi-classical direct ab initio MD method.