Unified assignment of alkyl C-H vibrational spectra of ethanol by molecular dynamics simulations

○ Lin Wang[1,2], Tatsuya Ishiyama[3], and Akihiro Morita[1,2]

[1] Department of Chemistry, Tohoku University, Japan
[2] ESICB, Kyoto University, Japan
[3] Department of Applied Chemistry, University of Toyama, Japan

[Introduction]

In the measurement of vibrational spectroscopy, the C-H stretching band of alkyl moieties (2800~3000 cm^{-1}) is one of the most widely observed bands to date. It is regarded as a fingerprint to investigate polymers, membranes, proteins, ionic liquids and so on. In order to investigate the details of molecular structure and dynamical processes from vibrational spectroscopies, correct assignment of the spectra is of indispensable importance. However, the C-H band is often troublesome to be interpreted as the overlapping peaks are congested in this region. It is too challenging to fully disentangle the complicated bands solely by experimental means. Reliable theoretical investigation can help extracting the rich spectral information.

In this work, we perform molecular dynamics (MD) simulations to calculate IR, Raman and sum frequency generation (SFG) spectra of ethanol. Although various vibrational spectroscopic studies have been carried out for gas and liquid ethanol, there still remain confusion in assignment of C-H stretching band of ethanol. With the help of MD simulations, it is possible to decouple the overlapping peaks in different ways (Figure 1) and assign each vibrational mode in IR, Raman and SFG spectra on a unified basis. This work will propose a systematic method to decouple overlapping bands and guide to further study of vibrational spectra of large organic molecules.
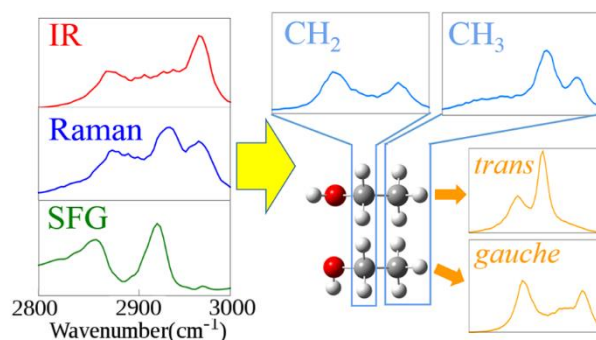

Fig. 1. Decomposing vibrational spectra into contribution from various C-H stretching

[Model and Method]

In reliable MD simulations of vibrational spectra, molecular modeling is of key importance. The model should be both flexible and polarizable. In this work, the flexible model is described by natural internal coordinates, while polarizable model is described by the charge response kernel (CRK) theory. We extend our modeling to allow for different conformers. The molecular parameters are accurately described for each conformer and are interchangeable by some large amplitude motion(s) in MD simulation.[1] The parameters are obtained by quantum mechanical (QM) calculations at the B3LYP/aug-cc-pVTZ level.

[Results and Discussion]

First, MD simulations for bulk ethanol liquid were carried out to validate the performance of the presented model. The calculated molecular properties, such as density and heat of vaporization, dipole moment and ratio of different conformer are in good agreement with experimental results.

IR and Raman spectra were also calculated and compared with experimental data. The calculated results show good agreement with experimental data in both ethanol (CH_3CH_2OH) and partially deuterated species (CH_3CD_2OH, CD_3CH_2OH). The influence of different conformer was investigated by performing MD simulations with pure *trans* or pure *gauche* ethanol.[2] The results (Figure 2) show that pure *trans* and *gauche* spectra provide similar peak positions and intensities with the original CH_3CD_2OH spectra (Panels (a, b)), indicating that the influence of *trans/gauche* conformer on the methyl vibrations at C_β position is small. On the other hand, the spectra of CD_3CH_2OH (Panels (c, d)) show clearly different shapes between *trans* and *gauche* conformers. These results indicate that the difference in *trans* and *gauche* conformers has large influence on the methylene vibrations at the C_α position.

The surface simulations were carried out to calculated SFG spectra. [2] The calculated SFG spectra under different polarization combination show good agreement with experimental data. Through short time correlation analysis, $Im[\chi^{(2)}]$ spectra was decomposed into contribution from *trans* and *gauche* conformer (Figure 3). In CH_3 spectra of Panels (a, b) the line shape of *trans* and *gauche* are quite analogous. In CH_2 spectra of Panels (c, d), however, *trans* and *gauche* exhibit clear different line shapes. The negative band at 2963 cm^{-1} (Panel (c)) is attributed to C-H stretching in gauche conformer. These results are consistent with IR and Raman assignment.
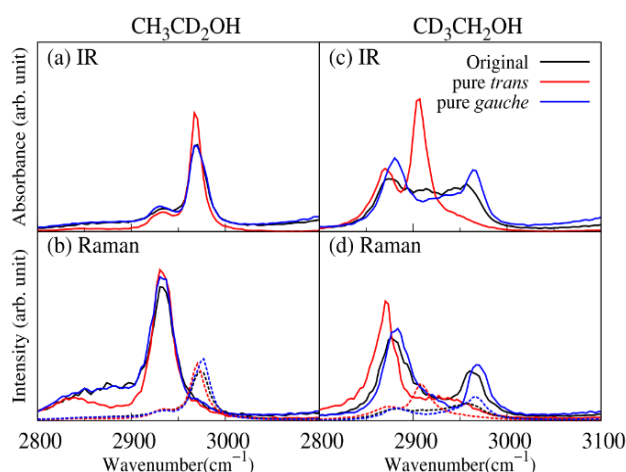

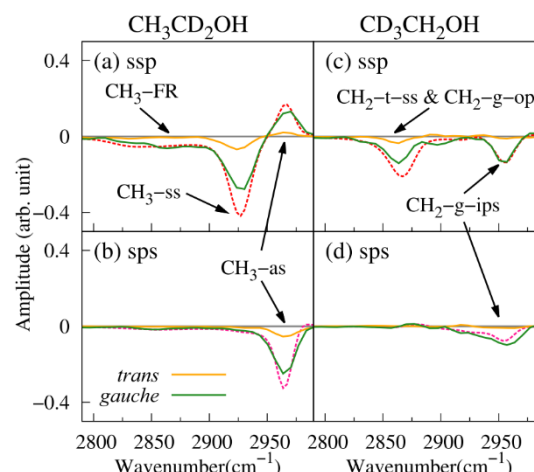Fig. 2. Calculated IR and Raman spectra of deuterated ethanol with pure *trans* or *gauche* conformer.

Fig. 3. Decomposed spectra of $Im[\chi^{(2)}]$ into the contribution from *tran* and *gauche* conformer

[References]

[1] L. Wang, T. Ishiyama, A. Morita. *J. Phys. Chem. A* submitted

[2] L. Wang, T. Ishiyama, A. Morita. *J. Phys. Chem. A* submitted