Vibrational Absorption Intensities Studied by the Linear and Nonlinear Response Functions of Conceptual DFT

Satoshi Yabushita

Department of Chemistry, Keio University, Yokohama, 223-8522, Japan

Theoretical understanding of electron density migration caused by a molecular structure change is of central importance in chemistry. From this viewpoint, we show our studies on the fundamental as well as overtone absorption intensities of CH and OH bonds. Their IR intensities reflect the structure dependence of molecular dipole moment functions (DMFs) caused by electron density migration.

We have analysed the following interesting characteristics.

1) In most molecules, fundamental (overtone) CH and OH stretching intensities are sensitive (insensitive) to the adjacent substituents.[1-4]
2) However, in some alcohols, we have seen fundamental (overtone) intensities show a weak (strong) conformation dependence.[1,5]
3) Formation of hydrogen-bonded complexes increases (decreases) OH stretching intensities.[5]

Based on the local mode model, we used the one-dimensional anharmonic vibrational wavefunctions $\{\varphi_v(\Delta R)\}$, and expressed the DMF vector of a particular molecule or conformer A as a polynomial $\boldsymbol{\mu}^A(\Delta R) = \sum_n \boldsymbol{M}_n^A \Delta R^n$, where ΔR is the bond displacement. With the graphical representations of these DMF expansion coefficients $\{\boldsymbol{M}_n^A\}$ and of the matrix elements $\langle \varphi_v | \Delta R^n | \varphi_0 \rangle$, each of the above characteristics can easily be explained as a interplay between the mechanical and electrical anharmonicities.[3,5] Furthrmore, using the linear and non-linear response functions of conceptual DFT, we express these coefficients $\{\boldsymbol{M}_n^A\}$ in terms of the first- and second-derivatives of the nuclear attractive potential and visualize electron density migration caused by molecular vibrations. We will also explain the reason why

4) polyynes ($C_{2n}H_2$, n=1-9) exhibit the unusually strong $\pi_g+\pi_u$ combination bands in the IR spectra.[6]

References

[1] K.Takahashi *et al.*, *JPCA*, **107**, 11092 (2003); [2] K.Takahashi *et al.*, *JPCA*, **109**, 4242 (2005); [3] H.Takahashi *et al*, *JPCA*, **117**, 5491 (2013); [4] H. Takahashi *et al*, *JPCA*, **119**, 4834 (2015) ［5］M. Tsuyuki *et al*, *JPCA*, **125**, 2101 (2021) ; [6] M. Tsuyuki *et al*, *JPCA*, **125**, 6404 (2021).