A study of factor affecting vibrational modes in quantum chemical computations and spectroscopy

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Abstract

Vibrational spectroscopy is based on vibrational transitions due to absorption and emission of electromagnetic radiations. Vibrational spectroscopic analysis provides a dynamic view of the molecule. Computational chemistry along with vibrational spectroscopy can provide experimentalists with precise information regarding the properties and behavior of materials. These techniques can help resolve issues that cannot be practically achieved due to instrumentation limits. The analysis of the Infrared (IR) and Raman spectra is now helpful not only for the structural characterization of molecular compounds, but also to derive detailed information on the electronic response from spectroscopic observables. There are various factors that should be taken into consideration while doing quantum chemical calculations. Purpose of the current study is to investigate important factors and their effect on the vibrational modes of a molecule during calculations.

Keywords: Spectroscopy, Raman, IR, FT-IR, Nonlinear optics, NLO, NLO materials, SHG, frequency doubling, polarizability, quantum chemistry, vibrational modes

Introduction

Vibrational spectroscopy provides precious information about the structural properties of molecules such as inter and intramolecular forces, hydrogen bonding, isomerism etc. Vibrational spectroscopy is based on vibrational transitions due to absorption and emission of electromagnetic radiations. These transitions are caused due to the vibrations of atoms constituting the molecule and appear in the waveumber range from 10^2 to 10^4 cm^{-1}. The vibrational energies of the molecule can be explored by infrared (IR) and Raman spectroscopy. The information provided by IR and Raman spectroscopic methods is often complementary. Thus to obtain complete vibrational analysis, both methods are necessarily be implemented [1-3]. By introducing the laser as a source for Raman and FT-IR spectrometers, vibrational spectroscopy has become a very powerful tool for the elucidation of molecular structure [4-5]. Vibrational spectroscopic analysis provides a dynamic view of the molecule. It has considerably contributed to the development of different areas such as polymer chemistry, fast reaction dynamics, catalysis and charge-transfer complexes [6]. The implementation of spectroscopy for exploring the structure of simple and

complex molecules has been of great value in the field of structural study of organic, inorganic and organo-metallic compounds, biological molecules, polymers and minerals [7-11].

Factors affecting vibrational modes

Intermolecular Hydrogen bonding

Hydrogen bonding is a donor-acceptor interaction involving hydrogen atom. According to the classical electrostatic model of hydrogen bonding (X-H⋯Y), because the electron density of Y exerts an attractive force on the proton and the approach of Y should always lengthen the X-H bond owing to the charge transfer that occurs from the proton acceptor Y to the proton donor, in particular to the X-H $\sigma*$ antibonding orbital, the X-H bond should be weakened upon the hydrogen-bond formation and concomitantly elongated. When a hydrogen bond complex X-H⋯Y is formed the following conspicuous changes are usually observed in the vibrational spectrum.

a) The X-H stretching wavenumber shifts to lower wavenumbers.
b) The breadth and intensity of the X-H stretching wavenumber increases markedly.
c) The X-H bending wavenumber shifts to higher wavenumbers with decreases in intensity.
d) Appearance of new vibrational bands corresponding to H⋯Y stretching and deformation at low wavenumbers
e) Shifting of the vibrational modes involving hydrogen bond acceptor group Y

In the last few years, the role of the weak C-H-O interactions in crystal engineering and molecular recognition processes has aroused considerable interest owing to their anomalous behaviour. The spectroscopic investigations of such interactions have shown that they can cause the shortening of the C-H bond distance along with the increase of C-H stretching wavenumber and is named 'blue-shifted hydrogen bonds". To rationalize the C-H shortening and the consequent blue shift of the C-H stretching wavenumbers, three explanations have been suggested. Hobza *et al.* proposed that the origin of the bond shortening is attributed in part to dispersion effects, but primarily to a two step mechanism that involves charge transfer from the proton acceptor to the remote part of the proton donor, causing it to structurally relax, which in turn leads to a shortening the C-H bond. Another explanation for the C-H bond shortening is the effect of the electric field exerted by the proton acceptor molecule. A recent explanation proposed for the C-H⋯O interactions expect that at the equilibrium geometry of a complex the attractive interactions must be balanced by repulsive forces. Electrostatic forces provide the dominant attractive interactions. Pauli repulsion (steric interactions) between the two fragments provides the balancing repulsive forces. This repulsion shortens the C-H bond and leads to the observed blue shift in the vibrational wavenumbers.

Hyperconjugation

It is the interaction of sigma (σ) orbital of a single bond with the pi (π) orbital of an adjacent double/triple bond. Hyperconjugation occurs with the releasing of electronic charge from σ_{C-H} to the C-C bond that connects the two interacting groups. The most evident effect of this interaction is that the C-C bond decreases in length from its normal value (1.54 A) and increases in strength, but effects of hyperconjugation can also be on C-H bonds. The different values of the equilibrium charges of hydrogen atoms involved in C-H bonds obtained from infrared intensities have been directly correlated to spectral patterns. When the hydrogen becomes more acidic due to the release of electronic charge, the C-H stretching intensity in IR decreases and the intensity of bending deformation mode increases. This will increase C-H bond ionicity and C-H bond strength.

Non-Bonded Interactions

The most important geometrical characteristics of non-bonded interaction is that, the distance between the non-bonded atoms is less than the sum of the van der Waals radii. These short contact interactions may be attractive or van der Waals repulsive. The van der Waals repulsion between two neighbouring hydrogen atoms in a chalcone molecule often causes twisting of phenyl ring as well as the rotation of functional groups. As a consequence of these interactions, the vibrational stretching wavenumbers of the the bands associated with the non-bonded interactions are shifted.

Intramolecular Charge transfer (ICT)

The compounds bearing the electron donor and electron acceptor at the end positions of the π-conjugated system is related to the existence of large intramolecular charge transfer responsible for second order NLO activity. The ICT causes the electron releasing effect in the acceptor moiety, affecting the spectral modes. For example C=C stretching mode of acceptor subunit occurs at lower wavenumber compared to the corresponding mode of the donor subunit. For the conjugated path, ICT induces large variation in the dipole moment as well as in the molecular polarizability simultaneously during vibration. This produces the IR and Raman activity for the same mode and hence comparable intensities of IR and Raman bands arising from the vibrations of conjugated system can be observed. The electron donating effect of donor unit also causes wavenumber shifting for the vibrations of the donor group.

Computational methods

Now days, methods in computational chemistry have become a key to investigate materials which are very far away from our reach. It also helps the researcher to know about the chemical systems before performing the

actual experiments. The quantum mechanics, classical mechanics as well as statistical physics and thermodynamics are the foundation bricks for most of the computational chemistry theory and the software associated with it. All important methods which are used in computational chemistry for calculating molecular properties and processes may broadly be divided in to three categories. [12-14]

a) Ab-initio methods-which uses Schrödinger's equation, but with approximations,

b) Semi-empirical methods - using experimental parameters and extensive simplifications of Schrödinger's equation

c) Molecular mechanics methods -is a classical approach which deals with bonds between the atoms in a molecule.

Conclusion

Vibrational spectroscopy is a very powerful tool for the study of molecular structure. Use of both the IR and Raman spectroscopy give complete picture of the vibrational modes of the molecule. There are various factors like intermolecular hydrogen bonding, hyperconsugation, non bonded interactions, inter molecular charge transfer which affect vibrational modes of the molecule. The inter molecular charge transfer ability of a molecule increases hyperpolarizability of the molecule. This induces large variation in the dipole moment as well as in the molecular polarizability simultaneously during vibration. Such molecules are suitable materials for nonlinear optics.

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