



Topical Perspectives

A comparative study on the experimental and calculated results of mid-infrared and Raman vibrational modes of nucleic acid bases

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ABSTRACT

The MIR (mid-infrared) and Raman spectra of the nucleic acid base powders were tested by Fourier transform infrared spectroscopy and laser Raman spectroscopy. The vibrational modes of nucleic acid base crystals were simulated by the generalized energy-based fragmentation approach under periodic boundary conditions (hereinafter referred as PBC-GEBF) together with Gaussian09 software. Taking into account the intermolecular hydrogen bonds in the unit cell and the weak interactions between the unit cells, the PBC-GEBF method adopted by our group was for the first time used for calculating nucleic acid base crystals in the 400–2000 cm^{-1} band. The theoretical and experimental spectra turn out to be in good agreement with each other. Compared with the calculated results of the nucleic acid base monomer, the calculated results of crystals appear to be in better agreement with the experimental results. Some weak vibration peaks were reproduced by simulation, and the positions of the vibration peaks agree well. By analyzing the vibrational modes, it can be observed that the vibrational modes below 1000 cm^{-1} are mainly characterized by the collective vibrations involving all the molecules in the unit cell. In addition to intramolecular interactions, weak intermolecular interactions (including Van der Waals force and weak hydrogen bond) and the lattice stacking force also contribute to the overall vibrations. This study is of great importance to the analysis of the stability of RNA/DNA structures and their genetic properties.

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1. Introduction

Nucleic acids are the essential biological macromolecules involved in the transfer and expression of the genetic information in cells. As the significant parts of nucleic acids, nucleic acid bases have major research value for studying organism heredity, evolution, variation and biological molecular activity. In this sense, it is indispensable to theoretically and experimentally delve into the spectral characteristics of nucleic acid bases.

Infrared spectrum is used to reflect the molecular vibration and rotation characteristics. It usually can be divided into three regions: the near-infrared (4000–12800 cm^{-1}), mid-infrared (200–4000 cm^{-1}) and far-infrared (10–200 cm^{-1}) region. Mid-infrared spectrum belongs to the fundamental vibrational spectrum of molecules, which can reveal the role of bases in the composition of biological macromolecules such as DNA/RNA, and

help further identify them. Raman spectrum, as a powerful supplement to the infrared spectrum, reflects symmetric vibrations and nonpolar group vibrations with no infrared active molecules. It can be used to study the structures and changes of biological macromolecules, and show weak absorption peaks that the infrared spectrum cannot do. It is worth mentioning that Raman spectroscopy can be used to eliminate the influence of water on the infrared spectrum, as water has very weak Raman absorption.

The application of Raman and infrared spectroscopy in nucleic acid bases has been reported in some literature [1–4]. So far, the calculation of the theoretical spectrum of the nucleic acid bases in the mid-infrared band still stays at the monomer level [5,6]. Using the vibration spectrum of the monomer model to study the crystal vibration spectrum ignores the influence of the external field environment. Therefore, it is necessary to calculate the vibration spectrum of crystals under periodic boundary conditions. Compared with the traditional periodic quantum chemistry method, the PBC-GEBF method is able to divide up the periodic system for a more specific study, and can obtain the vibration spectrum of crystals with a smaller calculation cost and better performance.

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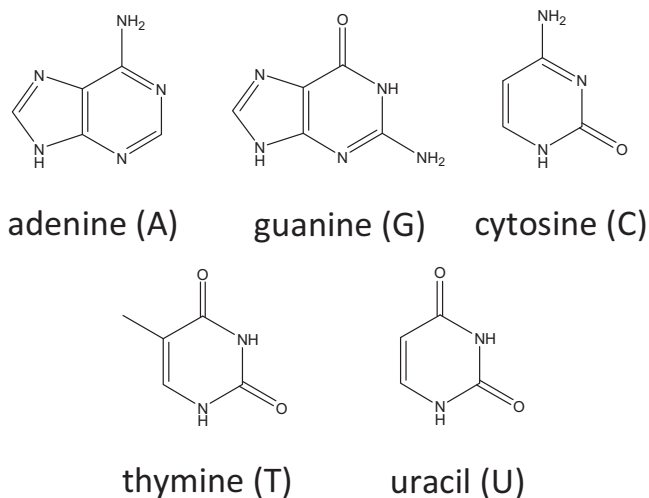


Fig. 1. Structures of nucleic acid bases: adenine, guanine, cytosine, thymine, uracil.

This paper studies the mid-infrared and Raman spectra of five nucleic acid bases (adenine, thymine, cytosine, guanine, uracil), with a comparison of the theoretical results and the experimental data. It turns out that the PBE–GEBF method and density functional theory (DFT) can well describe the lattice parameters of crystals, and provide the mid-infrared and Raman spectra which are in good agreement with the experimental measurements. This study lays a theoretical foundation for the further exploration of the structures of biological macromolecules such as nucleic acid molecules and DNA/RNA.

This paper starts with a brief outline of the experimental procedures in Section 1; Section 2 introduces the theoretical methods, followed by the measurement results and computational details in Section 3; after the presentation of the results and relevant analysis, the last section comes to a final conclusion.

2. Materials and methods

2.1. Materials and instruments

All the nucleic acid bases were white crystalline powder purchased from Sigma Aldrich Chemical Co, their structures shown in Fig. 1. The samples were used without further purification for spectrum measurement.

Mid-infrared absorption spectra were obtained by Bruker v80 Fourier transform infrared spectrometer under room temperature using DTGS detector, the frequency ranging between

400–2000 cm^{-1} , the spectral resolution 4 cm^{-1} and the single-noise ratio (SNR) higher than 50000:1. The sample spectra had a good consistency after several runs.

The Raman spectra in the 400–2000 cm^{-1} range were detected by Themor DXR532 laser Raman spectrometer. The Raman spectroscopy provided 0.1 mW precision with 780 nm diode laser under room temperature, the spatial resolution better than 1 μm , and the spectral reproducibility less than or equal to $\pm 0.2 \text{ cm}^{-1}$. The ONMIC software along with the instrument could help analyze and process the spectrum data.

2.2. Methods

The samples were mixed with KBr and pressed in between 13 mm thick slices before the mid-infrared spectrum testing. Repeated experiments rendered the perfect thickness (0.5 mm) and purity (samples: KBr = 1:10) of the samples. The sample absorption spectra were detected with KBr as reference. In order to avoid the

influence of the reference, the weight of KBr in the background must be consistent with the KBr in the samples.

The reception of Raman spectra was relatively simple, the process as follows: pure samples were put on one glass slide, covered with another slide, placed under the Raman microscope; then the focal length was adjusted for the best test point to complete the Raman spectrum detection.

The frequency calculations of nucleic acid bases were carried out based on the optimized structure to extract the intramolecular and intermolecular modes of vibration and rotation of the samples. Before calculating the vibration frequency, the unit cell geometries of nucleic acid bases were optimized by the DFT method using hybrid functional PBE(D3BJ) and a basis set augmented with one set of polarization functions 6-311++G(d,p), the monomer optimized by the DFT theoretical approach and B3LYP/6-311++G(d,p) parameter setup with the Gaussian 09 software.

The framework of generalized energy-based fragmentation (hereinafter referred as GEBF) approach was for the first time used to calculate the frequency features of nucleic acid bases. For the GEBF approach [7,8], the total energy of a given molecular system is formulated as a sum of ground-state energy of various “electrostatically embedded” subsystems. Each subsystem includes a few fragments, and the corresponding capping hydrogen atoms were immersed in the background point charges generated by all other atoms in the system. Very recently, its extension to the periodic system has been realized [9]. Two key factors have been taken into consideration in the employment of this approach. The first is the translational symmetry introduced by periodicity to check the uniqueness of the generated subsystems. The second is the ONIOM-type technique to minimize the computation of the “embedded subsystems”. Based upon the two simplifications, the total energy per unit cell of a molecular crystal is elegantly expressed as follows:

$$E_{\text{unit-cell}} = \sum_m^M C_m \tilde{E}_m - \left(\sum_m^M C_m \right) \sum_{A \in K(B>A) \in K} \sum_{B \in K} \frac{Q_A Q_B}{R_{AB}} + E_{\text{Ewald-sum}} \quad (1)$$

\tilde{E}_m stands for the ground-state energy of a given subsystem embedded in a finite array of point charges of a super cell (a cutoff distance 18 Å is used to define the super cell, denoted as K). C_m denotes the coefficient (a positive or negative integer, uniquely determined by the Inclusion and Exclusion Principle in mathematics) of this subsystem. Q_A, Q_B represents the atomic charge at atom A, B respectively. R_{AB} refers to the interatomic distance, and $E_{\text{Ewald-sum}}$ stands for the classical charge–charge interactions in the central cell and the charge–charge interactions between the central cell and all image cells, which can be accurately computed with the Ewald summation method.

Furthermore, the first-order derivatives of the total energy with respect to the atomic coordinates and lattice parameters have also been achieved [10]. In this regard, we can optimize the geometrical structures of molecular crystals. More details on how to generate subsystems and add boundary charges or atomic charges can be found in Ref [10]. Our method also allows the implementation of the field compensation scheme to take into account the polarization effect and long-range interactions. It is noticeable that the field compensation scheme can be applied to normal crystals without macroscopic electric polarization. In this paper, we aim to delve into the spectroscopic properties of DNA/RNA nucleobases, which entails second-order derivatives (Hessian) of the total energy in theory. And this has been done very recently with the PBC–GEBF approach [10].

For molecular crystals, we can write down the dynamic equation as follows:

$$m_A \ddot{R}_{A,L,\alpha} = - \sum_{L'} \sum_{A'} \sum_{\alpha'} R_{A',L',\alpha'} H_{A L \alpha, A' L' \alpha'} \quad (2)$$

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