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# QUALITATIVE AND QUANTITATIVE STUDY OF INTERMOLECULAR WEAK INTERACTIONS FOR BENZOIC ACID AND ANISIC ACID USING TERAHERTZ SPECTROSCOPY COMBINED WITH DFT

**Yueting Huang[a], Xianhua Yin[b] and Yuan Tang[b,*]**

[a]Department of Electronic Information Engineering, Guilin Institute of Information Technology, 541004 Guilin, China

[b]Guangxi Key Laboratory of Automatic Detecting Technology and Instruments, School of Electronic Engineering and Automation, Guilin University of Electronic Technology, 541004 Guilin, China

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*e-mail: tangyuan@guet.edu.cn

Supplementary Material

The following content describes how to use vibrational energy distribution analysis (VEDA) for potential energy distribution (PED) analysis and outlines the steps for using Multiwfn, version 3.8 dev (Beijing Kein Research Center for Natural Sciences, China), to calculate and analyze the interaction region indicator (IRI), energy decomposition analysis based on force-field (EDA-FF), and electrostatic potential (ESP). It should be noted that the methods and implementation steps used were proposed by Lu and Chen,[1] and this is hereby explained.

**Steps for PED analysis using VEDA**

1. Preparation work. Gaussian calculation: first use Gaussian to perform freq calculation, and rename the resulting ". fch" file to file1.fmu.
2. Start VEDA and load the file. Start the VEDA program and select the "file1.fmu" file from the corresponding directory.
3. Create and view DD2 file. Select Create. DD2 in the main window to generate the "skra.dd2" file.
4. Calculate and generate result files. Click the calculate button to generate "file1.ved" and "file1.vd" files.
5. View result file:

(1) ". ved" file: click the view ". ved" button directly to view, which records the proportion of each internal coordinate participating in each normal vibration mode. Rows represent the normal vibration mode number, and columns represent the internal coordinate number.

(2) ". vd" file: the information corresponds to ". ved", but only lists the main internal coordinates of each vibration mode, making it easier to read. The first column is the frequency of the normal vibration mode, followed by the internal coordinate number starting with 's', followed by the percentage contribution of the internal coordinate. The second half of the file also records the contribution of each internal coordinate to each normal vibration mode.

6. Identify the normal vibration mode. Based on the analysis of PED, the main components of the normal vibration mode and the definition of the current internal coordinates, combined with the molecular vibration animation displayed by GaussView, attempt to identify the normal vibration mode. Do not forcefully identify vibration modes that are too complex and difficult to accurately identify.

**Steps for calculating and analyzing IRI, EDA-FF, and ESP using Multiwfn (taking benzoic acid as an example)**

*1. Steps for implementing IRI method*

1.1 Prepare Gaussian output files and convert them into ". fch" format files

Use Gaussian to calculate benzoic acid, ensuring that the output file contains all the necessary information. Convert the Gaussian output file to ". fch" format and name it "benzoic_acid.fch".

1.2 Start "Multiwfn" and input the ". fch" file

Launch “Multiwfn” software. In the command line interface of “Multiwfn”, enter “benzoic_acid.fch” to load the file.

1.3 Select the weak interaction visualization analysis function and choose IRI analysis

In the main menu of “Multiwfn”, select the option related to visualizing weak interactions. Further select IRI (independent gradient model) analysis function.

1.4 Manually setting grid points (such as high-quality grid points)

Set the lattice spacing as needed. For small molecule systems such as benzoic acid, it is recommended to use a lattice spacing of 0.08 Bohr to obtain more accurate results.

1.5 Calculate and generate grid point files

Run calculations to generate grid point files for IRI analysis.

1.6 Preparation of VMD and drawing script

Copy the generated grid point files (such as “func1.cub”, “func2.cub”) and the “IRIfill.vmd” script file from the examples folder in the “Multiwfn” installation directory to the installation path of the VMD software.

1.7 Visualization of IRI results using VMD

(1) Start the VMD software, load the grid point file, and use the “IRIfill.vmd” script for visualization.

(2) Analyze the color correspondence of IRI iso-surface with $\text{sign}(\lambda_2)\rho$ value to distinguish covalent bonds, hydrogen bonds, van der Waals interactions, etc.

*2. Implementation steps of EDA-FF method*

2.1 Molecular pretreatment and fragment splitting

(1) Open the Gaussian output file of benzoic acid using GaussView and confirm the continuity of atomic numbers.

(2) Split benzoic acid molecules into specified fragments (such as each molecule is defined as a fragment) and save them as independent files one by one.

2.2 Fragment structure optimization

(1) Modify the calculation keywords of each fragment file, retaining only the structure optimization part.

(2) Optimize the structure of each segment using Gaussian and obtain the corresponding output file.

2.3 Atomic information organization

(1) Assign atomic types to each fragment using GaussView and export as a text file.

(2) Use Multiwfn to calculate the atomic charges of each fragment and add them to the corresponding text file.

(3) Summarize the atomic information file paths of all fragments and generate a molecular list file.

2.4 Perform EDA-FF analysis

Start Multiwfn and load the main file of benzoic acid. Select the “Energy Decomposition” and “Force Field Based Decomposition” function in sequence. Import the molecular list file and define the atomic number range for each fragment. Run calculations and output energy decomposition results.

*3. Steps for implementing ESP method*

3.1 Preliminary configuration

Copy the “. bat” and “. txt” files from “examples \ drawESP” in the Multiwfn installation directory to the directory where the Multiwfn executable file is located, and modify the VMD path in the. bat file to the actual path. Copy the “. vmd” file from this directory to the VMD installation directory, and add the specified proc statement at the end of the VMD “vmd.rc” file.

3.2 Document preparation

Retrieve the wave function file of benzoic acid (i.e., “. benzoic_acid.fch” copy the “. vmd” file from this directory to the VMD installation directory, and add the specified proc statement at the end of the VMD “vmd.rc” file) and place it in the directory where the Multiwfn executable file is located.

3.3 Generate necessary files for drawing

(1) Draw a surface vertex shading style diagram: double click “ESPpt.bat” (or “ESPext.bat” if extreme points are needed) to automatically generate “. pdb” files related to molecular structure, surface vertices (and extreme points), and copy them to the VMD directory.

(2) Draw an electronic density contour coloring style map: double click “ESPiso.bat” to automatically generate electron density and electrostatic potential related “. cub” files, and copy them to the VMD directory.

3.4 VMD drawing and optimization

(1) Draw a single molecular graph: start VMD, enter “pt” (surface vertex style) or “iso” (iso-surface style), and if extreme points need to be displayed, enter extra “ext”.

(2) Draw a molecular penetration map (if benzoic acid interacts with other molecules): start VMD, enter “pt2” (surface vertex style) or “iso2” (iso-surface style), automatically load multiple molecular files and display the penetration effect.

(3) Adjust the color scale, surface transparency, point size and other parameters in VMD, or use the Tachyon renderer to optimize the image effect.

## REFERENCES

1. Lu, T.; Chen, Q.; *ChemRxiv*, 2021. [Crossref]