Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary materials for

Fragment Quantum Chemical Approach to Geometry Optimization and Vibrational Spectrum Calculation of Proteins

Jinfeng Liu[1], John Z.H. Zhang[1,2,3] and Xiao He[1,2]*

[1]State Key Laboratory of Precision Spectroscopy, Institute of Theoretical and Computational Science, College of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062, China

[2]NYU-ECNU Center for Computational Chemistry at NYU Shanghai, Shanghai, 200062, China

[3]Department of Chemistry, New York University, NY, NY 10003, US

[*] To whom correspondence should be addressed: xiaohe@phy.ecnu.edu.cn

The computed vibrational frequencies (ν_i) were employed to evaluate the zero-point vibrational energy as follows

$$E_{ZPE} = \sum_{i=1}^{N_f} \frac{1}{2} h\nu_i \qquad \text{(S1)}$$

Various thermochemistry data (together with the translational and rotational partition functions), such as enthalpy, entropy, Gibbs free energy, etc. can also be calculated using the vibrational frequencies. The internal thermal energy resulting from the vibrational, translational and rotational motion of a molecule can be obtained from

$$E_T = E_{T,vib} + E_{T,trans} + E_{T,rot} = R\sum_{i=1}^{N_f} \Theta_{\nu_i} T\left(\frac{1}{2} + \frac{1}{e^{\Theta_{\nu_i}} - 1}\right) + \frac{3}{2}RT + \frac{3}{2}RT \qquad \text{(S2)}$$

where $\Theta_{\nu_i} = \dfrac{h\nu_i}{k_B T}$.

The constant volume heat capacity and entropy can also be obtained as follows

$$C_V = C_{V,vib} + C_{V,trans} + C_{V,rot} = R\sum_{i=1}^{N_f} e^{\Theta_{\nu_i}} \left(\frac{\Theta_{\nu_i}}{e^{\Theta_{\nu_i}} - 1}\right)^2 + \frac{3}{2}R + \frac{3}{2}R \qquad \text{(S3)}$$

$$S = S_{vib} + S_{trans} + S_{rot} = R\sum_{i=1}^{N_f} \left(\frac{\Theta_{\nu_i}}{e^{\Theta_{\nu_i}} - 1} - \ln\left(1 - e^{-\Theta_{\nu_i}}\right)\right) + R\left(\ln q_t + \frac{5}{2}\right) + R\left(\ln q_r + \frac{3}{2}\right) \qquad \text{(S4)}$$

where q_t and q_r are the translational and rotational partition functions, respectively. The enthalpy and Gibbs free energy can be obtained by evaluating

$$H = E_T + PV \qquad \text{(S5)}$$

$$G = H - TS \qquad \text{(S6)}$$

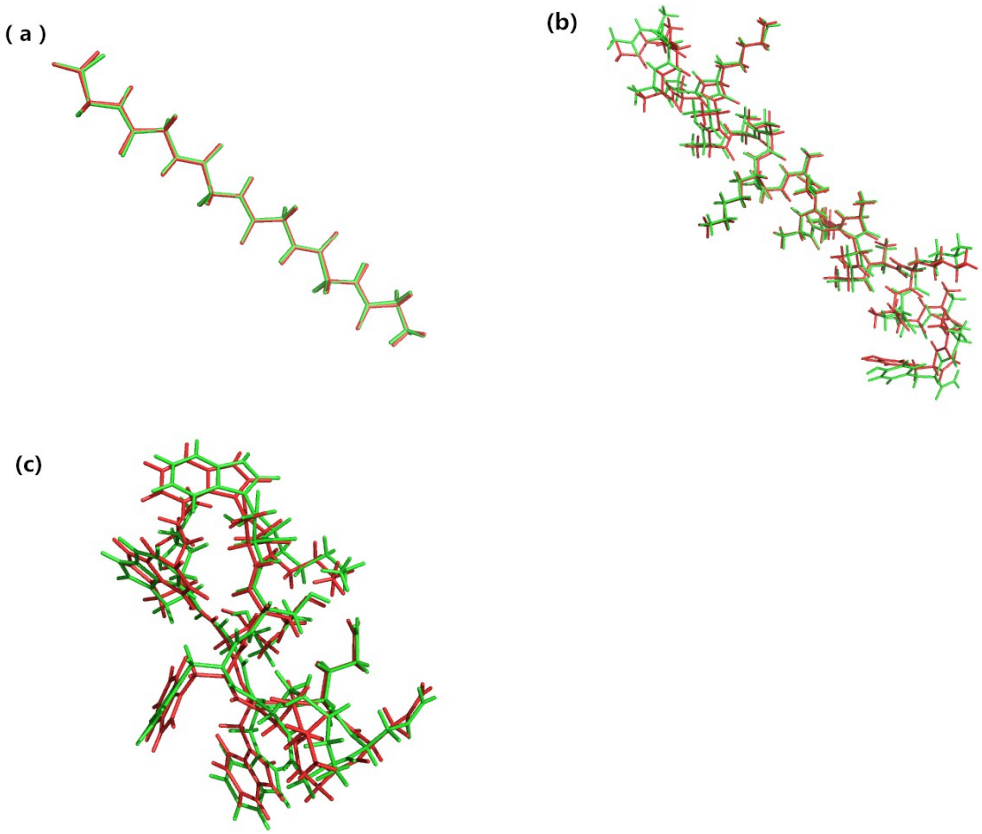


Figure S1. Superimposed (a) $(GLY)_6$, (b) AKA and (c) Trpzip2 structures optimized using EE-GMFCC at the HF/6-31G* level (green) with their corresponding initial structures (red).

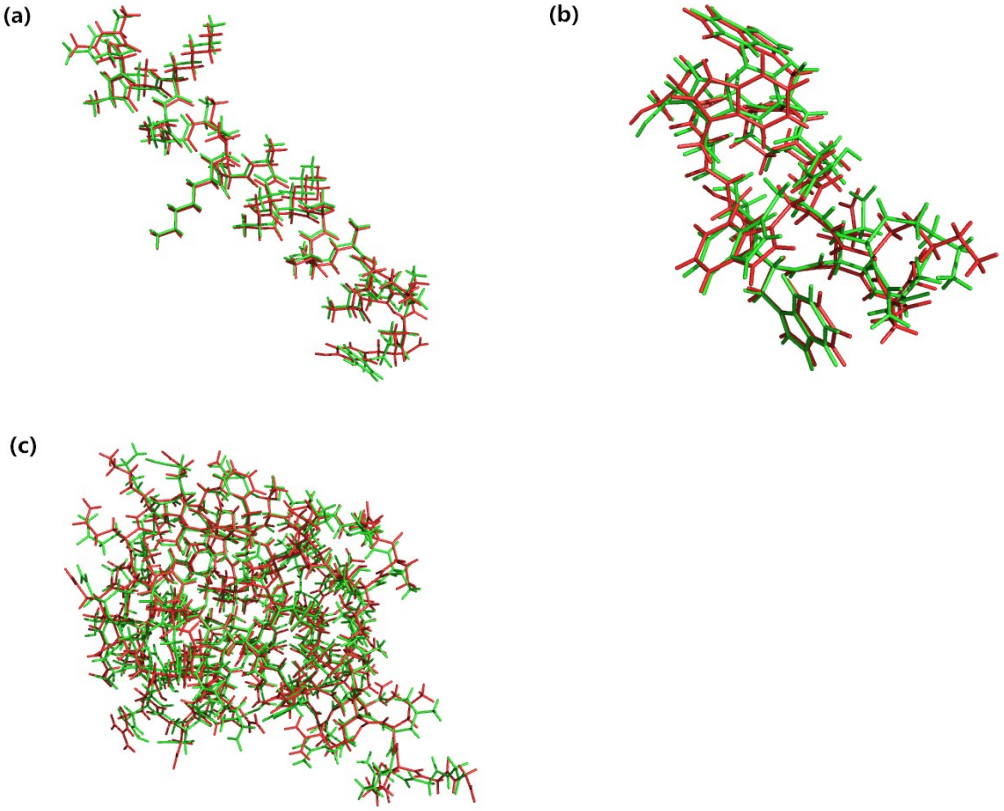
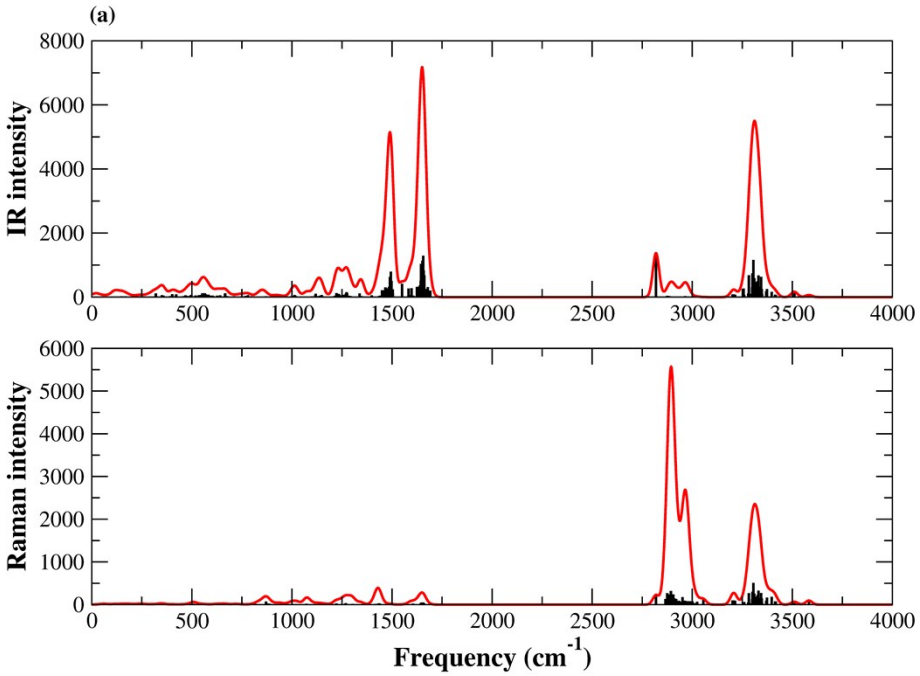
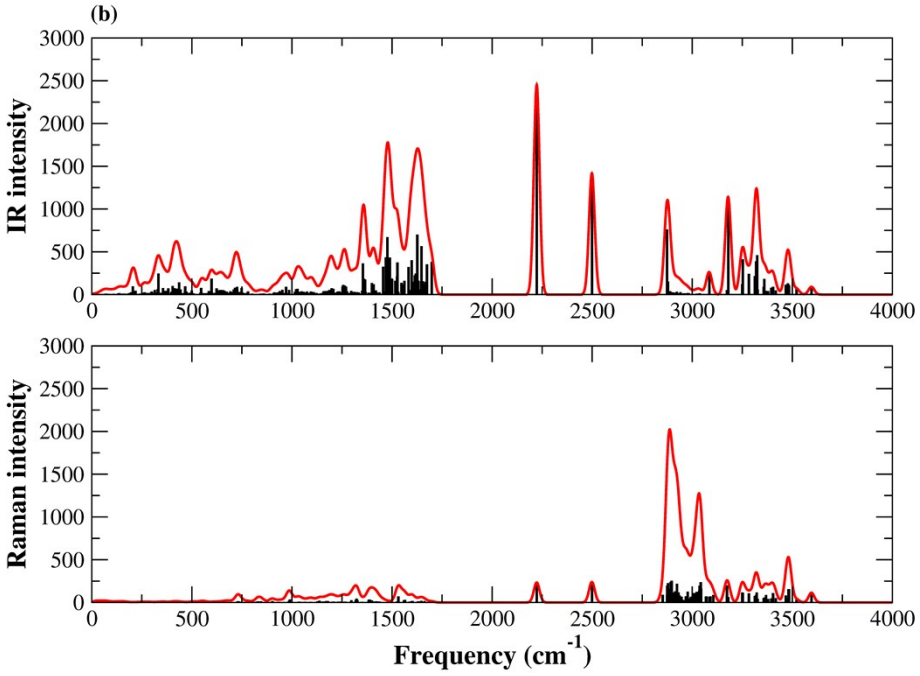


Figure S2. Superimposed (a) AKA, (b) Trpzip2 and (c) Ubiquitin structures optimized using EE-GMFCC at the M05-2X/6-31G* level (green) with their corresponding initial structures (red).


(a)
IR intensity
Raman intensity
Frequency (cm-1)


(b)
IR intensity
Raman intensity
Frequency (cm-1)

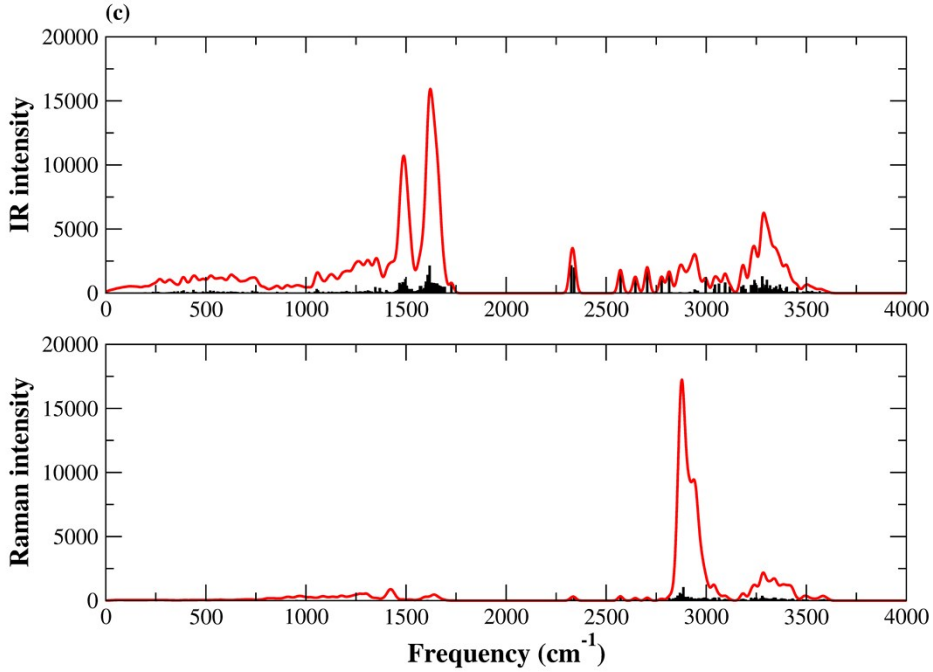


Figure S3. The calculated IR and Raman spectra for (a) AKA, (b) Trpzip2 and (c) Ubiquitin at the M05-2X/6-31G* level.