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

Supporting Information

Raman Optical Activity of Tetra-alanine in the Poly(L-proline) II Type Peptide Conformation

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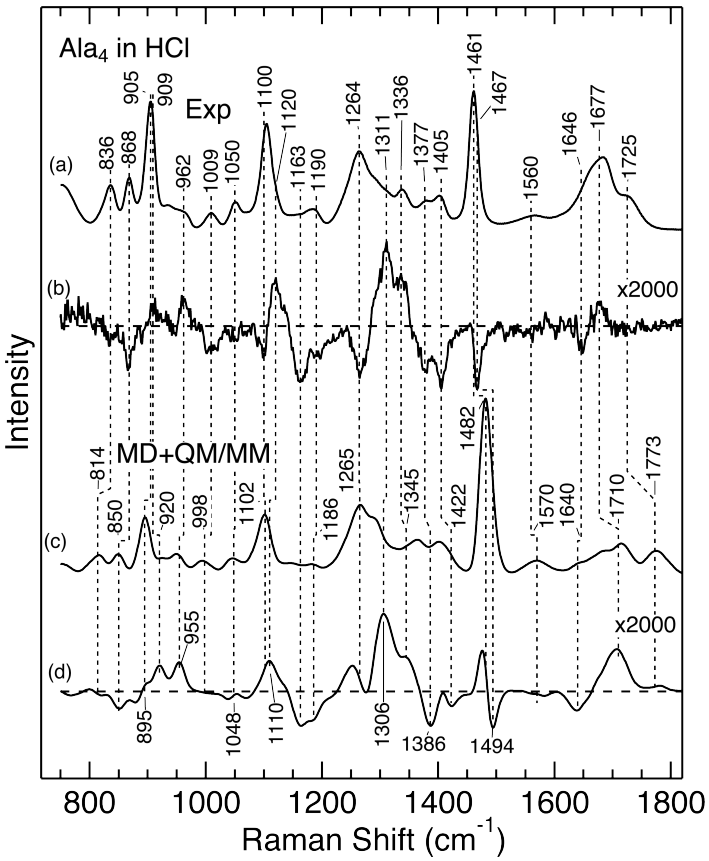

Figure S1. Observed and calculated Raman and ROA spectra of Ala_4 in 1 M HCl. The observed Raman (a) and ROA (b) spectra are shown. The Raman (c) and ROA (d) spectra determined using MD + QM/MM calculations are also shown. The ROA spectra are magnified by a factor of 2000.

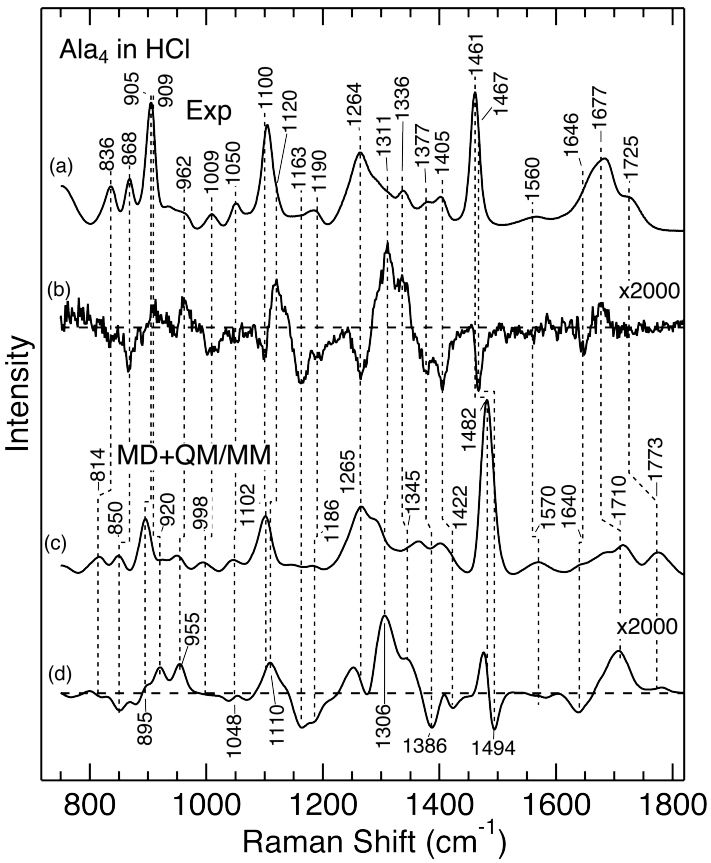

Figure S2. Observed and calculated Raman and ROA spectra of Ala_4 in 1 M DCl. The observed Raman (a) and ROA (b) spectra as well as the simulated Raman (c) and ROA (d) spectra are shown. The ROA spectra are magnified by a factor of 2000.

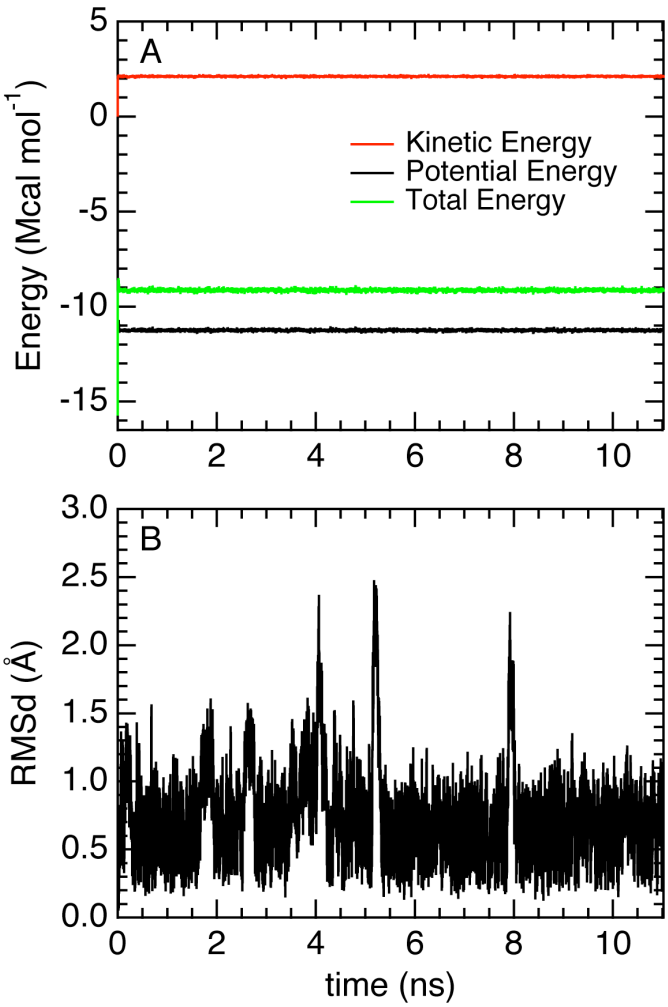

Figure S3. The time dependence of (A) energies and (B) root-mean-square deviation (RMSd) of cationic Ala_4 obtained by the 11 ns MD run. (A) Kinetic energy (red), potential energy (black), and total energy (green). (B) The RMSd of the Ala_4 backbone atoms (N, C^{α}, and C) from the initial structure.

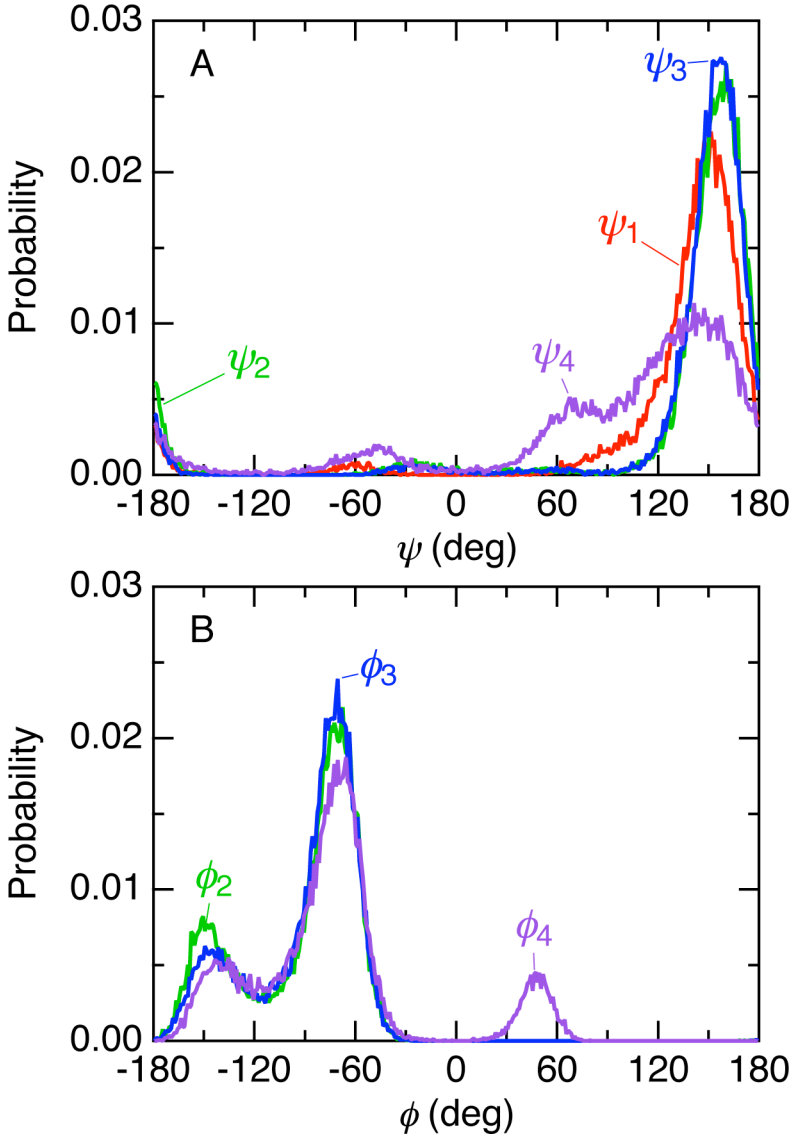

Figure S4. Probability distributions for the (A) ψ and (B) ϕ dihedral angles for cationic Ala_4 from the last 10 ns MD run.

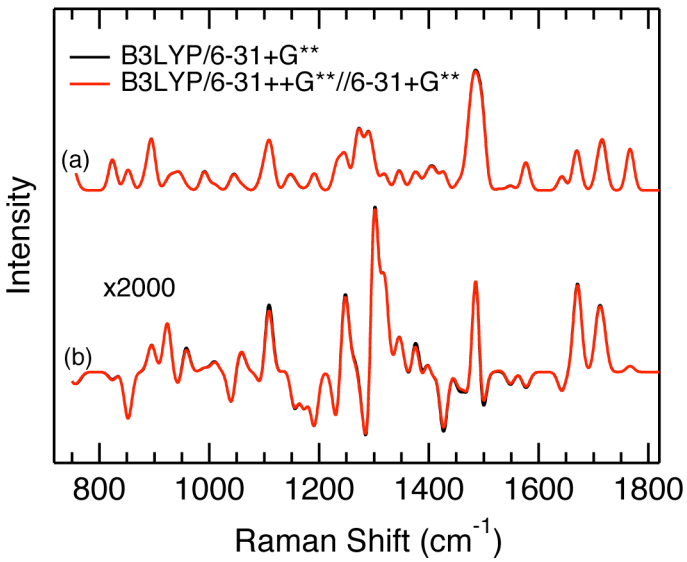

Figure S5. Raman and ROA spectra of cationic Ala_4 obtained by the QM/MM method based on a MD snapshot at 4.58 ns. The spectra drawn in black were computed by a B3LYP/6-31+G** level of theory. For the spectra drawn in red, Raman and ROA intensities were calculated by B3LYP/6-31++G**, while B3LYP/6-31+G** was used for the geometry optimization and force field calculation.

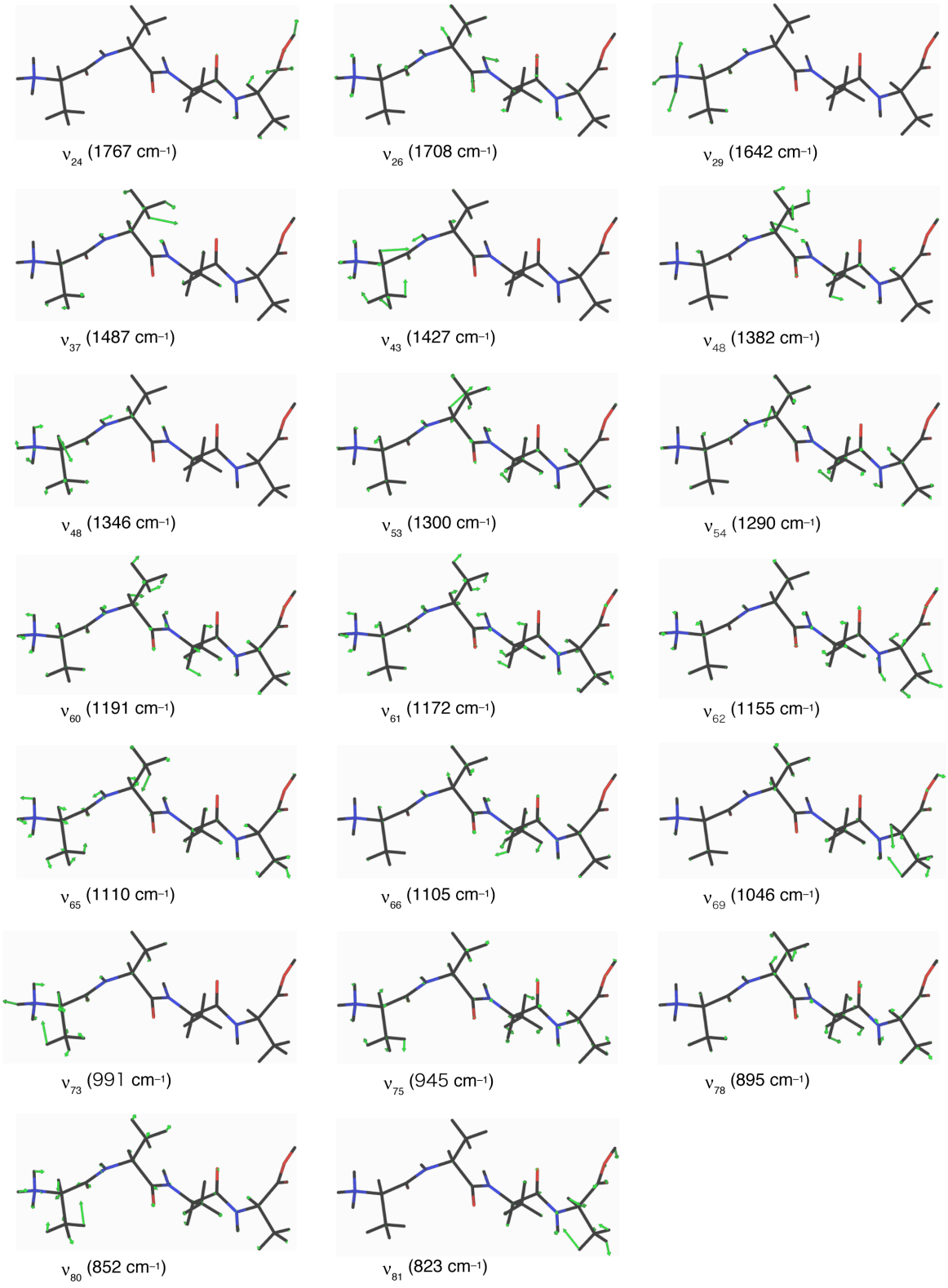

Figure S6. Atomic displacement vectors for selected vibrational modes for conformer 1, which is based on a MD snapshot at 4.58 ns.

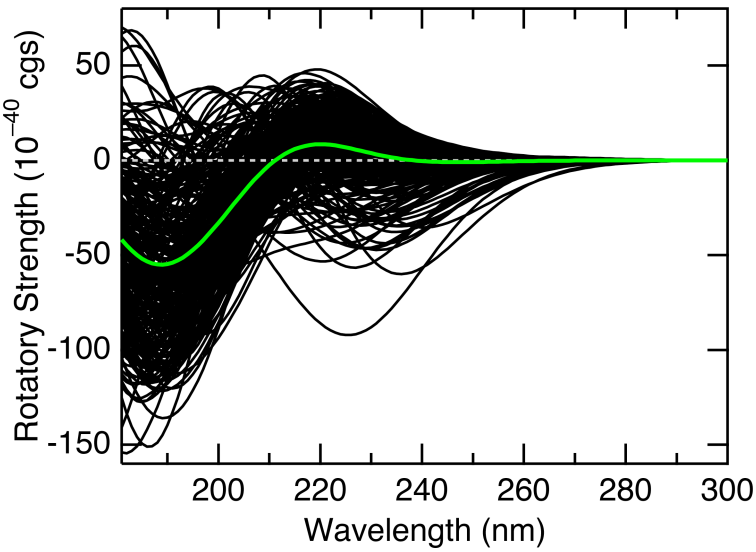

Figure S7. Calculated electronic circular dichroism spectra of cationic Ala_4. The spectra are calculated based on the MD + QM/MM method. The averaged spectra are shown in green, and the calculated spectra for 250 conformations are shown in black.

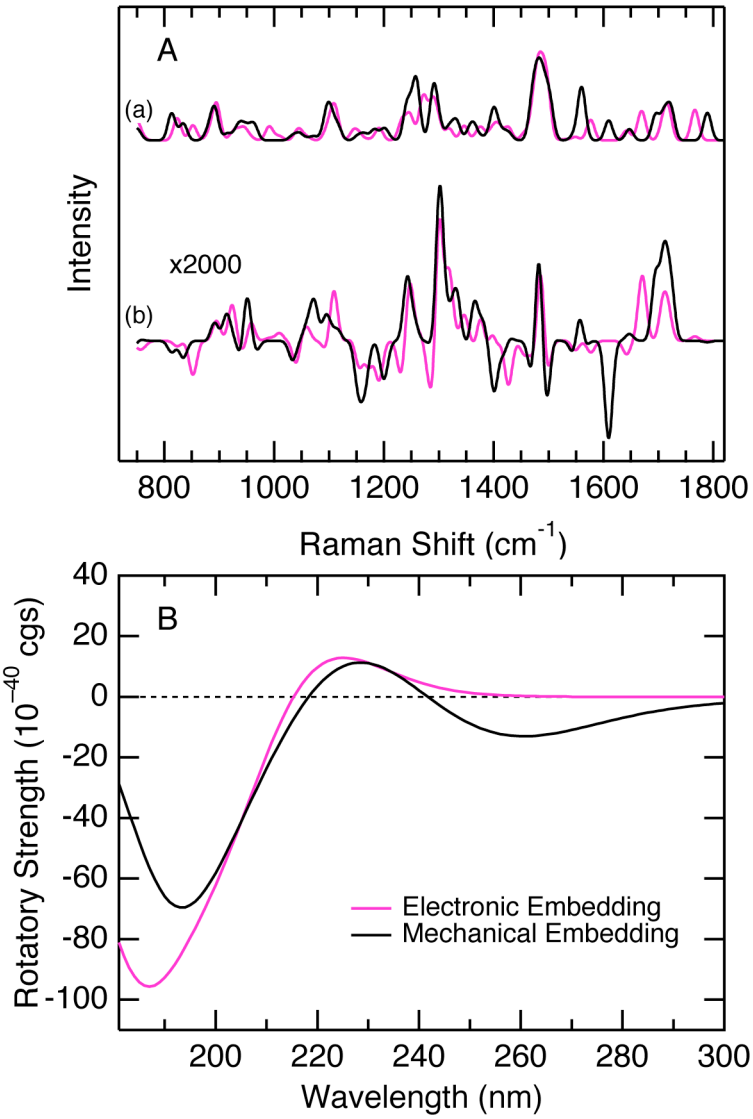

Figure S8. Effects of electrostatic interactions with surrounding water environments on the Raman, ROA, and ECD spectra of cationic Ala_4 based on a MD snapshot at 4.58 ns. (A) The (a) Raman and (b) ROA spectra drawn in black were obtained by the QM/MM method with the ME scheme for both geometry optimization and a computation of the spectra. On the other hand, the spectra shown in magenta were computed by the QM/MM method using the EE scheme. (B) ECD spectra of $Alal_4$ were calculated by the ME (black) and EE (magenta) scheme. For these cases, same optimized structure obtained by the QM/MM method using the EE scheme was chosen.

Table S1: Selected Dihedral Angles (deg) ofAla_4 based on a MD snapshot at 4.58 ns.

	ψ_1	ϕ_2	ψ_2	ϕ_3	ψ_3	ϕ_4	ψ_4
EE[a]	142.9	-74.5	143.2	-72.4	158.1	-67.6	136.7
ME[b]	148.4	-71.8	144.8	-74.5	160.2	-66.9	134.7

[a]An optimized structure with the electronic embedding (EE) scheme. [b]An optimized structure with the mechanical embedding (ME) scheme.