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

Supplemental information for
Simulations of infrared and Raman spectra in solution using the fragment molecular orbital method

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1 Description

Here, some details of derivations and additional results are provided.

2 Derivative of Energy with respect to a nuclear coordinate

The total energy for PCM without fragmentation is [1]

$$E = 2\sum_{i}^{\text{occ}} h_{ii} + \sum_{i}^{\text{occ}}\sum_{j}^{\text{occ}} [2(ii|jj) - (ij|ij)] + E_{\text{NR}} + \frac{1}{2}\sum_{t}^{N_{\text{TS}}} q_t V_t. \tag{1}$$

The derivative of the energy with respect to a nuclear coordinate is

$$\frac{\partial E}{\partial a} = 2\sum_{i}^{\text{occ}} h_{ii}^{a} + \sum_{i}^{\text{occ}}\sum_{j}^{\text{occ}} [2(ii|jj)^{a} - (ij|ij)^{a}] + \sum_{m}^{\text{all}}\sum_{i}^{\text{occ}} 4U_{mi}^{a} F_{mi} + E_{\text{NR}}^{a} + \frac{1}{2}\sum_{t}^{N_{\text{TS}}} \frac{\partial\left(q_t V_t\right)}{\partial a}. \tag{2}$$

The derivative of PCM specific term $W = \mathbf{V} \cdot \mathbf{q}/2$ is

$$\begin{aligned}
\frac{\partial W}{\partial a} =& \frac{1}{2} \sum_{t}^{N_{\mathrm{TS}}} \left[q_t \frac{\partial \left(V_t \right)}{\partial a} + V_t \frac{\partial \left(q_t \right)}{\partial a} \right] \\
=& V_{\mathrm{NR}}^a + \sum_{\mu,\nu} D_{\mu\nu} W_{\mu\nu}^a + 4 \sum_{m}^{\mathrm{all}} \sum_{i}^{\mathrm{occ}} U_{mi}^a W_{mi} + \sum_{t,s}^{N_{\mathrm{TS}}} q_t \frac{\partial C_{ts}}{\partial a} q_s, \qquad (3)
\end{aligned}$$

$$W_{\mu\nu}^a = \sum_{t}^{N_{\mathrm{TS}}} q_t \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R_t}|} \right| \nu \right\rangle^a \qquad (4)$$

$$W_{mi} = \sum_{t}^{N_{\mathrm{TS}}} q_t \left\langle m \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| i \right\rangle \qquad (5)$$

$$V_{\mathrm{NR}}^a = \sum_{t}^{N_{\mathrm{TS}}} \sum_{A} q_t \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right). \qquad (6)$$

Therefore, the derivative of the energy is

$$\begin{aligned}
\frac{\partial E}{\partial a} =& 2 \sum_{i}^{\mathrm{occ}} h_{ii}^a + \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} \left[2(ii|jj)^a - (ij|ij)^a \right] - \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} 2 S_{ij}^a \tilde{F}_{ij} + E_{\mathrm{NR}}^a \\
& + V_{\mathrm{NR}}^a + \sum_{\mu,\nu} D_{\mu\nu} W_{\mu\nu}^a + \frac{1}{2} \sum_{t,s}^{N_{\mathrm{TS}}} q_t \frac{\partial C_{ts}}{\partial a} q_s. \qquad (7)
\end{aligned}$$

3 Second order derivative of the energy

$$\begin{aligned}
\frac{\partial^2 E}{\partial a \partial b} =& 2 \sum_{i}^{\mathrm{occ}} h_{ii}^{ab} + \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} \left[2(ii|jj)^{ab} - (ij|ij)^{ab} \right] + \sum_{m}^{\mathrm{all}} \sum_{i}^{\mathrm{occ}} 4 U_{mi}^b F_{mi}^a \\
& - \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} 2 S_{ij}^{ab} \tilde{F}_{ij} - \sum_{m}^{\mathrm{all}} \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} 4 U_{mi}^b S_{mj}^a \tilde{F}_{ij} - \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} 2 S_{ij}^a \frac{\partial \tilde{F}_{ij}}{\partial b} + E_{\mathrm{NR}}^{ab} \\
& + \frac{\partial \left(V_{\mathrm{NR}}^a \right)}{\partial b} + \sum_{m}^{\mathrm{all}} \sum_{i}^{\mathrm{occ}} 4 U_{mi}^b W_{mi}^a + \sum_{\mu,\nu} D_{\mu\nu} \frac{\partial W_{\mu\nu}^a}{\partial b} + \frac{1}{2} \sum_{t,s}^{N_{\mathrm{TS}}} \frac{\partial}{\partial b} \left(q_t \frac{\partial C_{ts}}{\partial a} q_s \right). \qquad (8)
\end{aligned}$$

The derivative of the Fock matrix is

$$\frac{\partial \tilde{F}_{ij}}{\partial b} = F_{ij}^b + \frac{\partial F_{ij}}{\partial b} + \frac{\partial W_{ij}}{\partial b} \tag{9}$$

$$\frac{\partial F_{ij}}{\partial b} = h_{ij}^b + \sum_k^{\text{occ}} [2(ij|kk) - (ik|jk)]^b + \sum_m^{\text{all}} U_{mj}^b F_{mi} + \sum_m^{\text{all}} U_{mi}^b F_{mj} + \sum_k^{\text{all}} \sum_l^{\text{occ}} U_{kl}^b A_{ij,kl} \tag{10}$$

$$\begin{aligned}\frac{\partial W_{ij}}{\partial b} &= \sum_m^{\text{all}} U_{mi}^b W_{mj} + \sum_m^{\text{all}} U_{mi}^b W_{mj} + W_{ij}^b + \sum_t^{N_{\text{TS}}} \frac{\partial q_t}{\partial b} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle \\
&= \sum_m^{\text{all}} U_{mi}^b W_{mj} + \sum_m^{\text{all}} U_{mi}^b W_{mj} + W_{ij}^b - \sum_{t,s}^{N_{\text{TS}}} \sum_A C_{ts}^{-1} \left(\frac{Z_A}{|\mathrm{R}_A - \mathrm{R}_s|} \right)^b \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle \\
&- \sum_{\mu,\nu} \sum_{t,s}^{N_{\text{TS}}} D_{\mu\nu} C_{ts}^{-1} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| \nu \right\rangle^b \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle \\
&+ \sum_k^{\text{all}} \sum_l^{\text{occ}} U_{kl}^b A_{ij,kl}^{\text{PCM}} - \sum_{s,t,u}^{N_{\text{TS}}} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle\end{aligned} \tag{11}$$

$$A_{ij,kl}^{\text{PCM}} = 4 \sum_{t,s}^{N_{\text{TS}}} C_{ts}^{-1} \left\langle k \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| l \right\rangle \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle, \tag{12}$$

the derivative of V_{NR}^a is

$$\begin{aligned}\frac{\partial V_{\text{NR}}^a}{\partial b} = &- \sum_m^{\text{all}} \sum_i^{\text{occ}} \sum_{t,s}^{N_{\text{TS}}} \sum_A 4 C_{ts}^{-1} U_{mi}^b \left\langle m \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| i \right\rangle \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&- \sum_{\mu,\nu} \sum_{t,s}^{N_{\text{TS}}} \sum_A C_{ts}^{-1} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| \nu \right\rangle^b \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&- \sum_{\mu,\nu} \sum_{t,s}^{N_{\text{TS}}} \sum_{A,B} C_{ts}^{-1} \frac{\partial}{\partial b} \left(\frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_s|} \right) \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&+ \sum_{t,s}^{N_{\text{TS}}} \sum_A q_t \frac{\partial^2}{\partial a \partial b} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) - \sum_{s,t,u}^{N_{\text{TS}}} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right),\end{aligned} \tag{13}$$

and the derivative of $W^a_{\mu\nu}$ is

$$\begin{aligned}
\frac{\partial W^a_{\mu\nu}}{\partial b} &= \sum_t^{N_{\mathrm{TS}}} \frac{\partial q_t}{\partial b} \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^a + \sum_t^{N_{\mathrm{TS}}} q_t \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^{ab} \\
&= -\sum_{t,s}^{N_{\mathrm{TS}}} \sum_{\lambda,\sigma} C^{-1}_{ts} D_{\lambda\sigma} \left\langle \lambda \left| \frac{-1}{|\mathbf{r}-\mathbf{R_s}|} \right| \sigma \right\rangle^b \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^a \\
&\quad -4 \sum_{t,s}^{N_{\mathrm{TS}}} \sum_m^{\mathrm{all}} \sum_i^{\mathrm{occ}} C^{-1}_{ts} U^b_{mi} \left\langle m \left| \frac{-1}{|\mathbf{r}-\mathbf{R_s}|} \right| i \right\rangle \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^a \\
&\quad - \sum_{t,s}^{N_{\mathrm{TS}}} \sum_B C^{-1}_{ts} \frac{\partial}{\partial b} \left(\frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_t|} \right) \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^a \\
&\quad + \sum_t^{N_{\mathrm{TS}}} q_t \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^{ab} - \sum_{s,t,u}^{N_{\mathrm{TS}}} q_s \frac{\partial C_{su}}{\partial b} C^{-1}_{ut} \left\langle \mu \left| \frac{-1}{|\mathbf{r}-\mathbf{R_t}|} \right| \nu \right\rangle^a .
\end{aligned} \tag{14}$$

Therefore, the second order derivative of the energy is

$$\begin{aligned}
\frac{\partial^2 E}{\partial a \partial b} &= \sum_i^{\mathrm{occ}} \left[h^{ab}_{ii} + F^{ab}_{ii} - S^{ab}_{ii} \epsilon_i \right] + E^{ab}_{\mathrm{NR}} + \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{occ}} 4 S^b_{ij} S^a_{ij} \epsilon_i \\
&\quad + \sum_m^{\mathrm{vir}} \sum_i^{\mathrm{occ}} U^b_{mi} \left[4F^a_{mi} + 4W^a_{mi} - 4S^a_{mi}\epsilon_i - 2 \sum_k^{\mathrm{occ}} \sum_l^{\mathrm{occ}} S^a_{kl} A_{mi,kl} \right] \\
&\quad - \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{occ}} S^b_{ij} \left[2F^a_{ij} + 2W^a_{ij} - \frac{1}{2} \sum_k^{\mathrm{occ}} \sum_l^{\mathrm{occ}} S^b_{kl} A_{ij,kl} \right] \\
&\quad - \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{occ}} S^a_{ij} \left[2F^b_{ij} - \frac{1}{2} \sum_k^{\mathrm{occ}} \sum_l^{\mathrm{occ}} S^b_{kl} A_{ij,kl} \right] \\
&\quad - \sum_{i,j}^{\mathrm{occ}} \sum_{\lambda,\sigma} 2 S^a_{ij} C_{\lambda i} C_{\sigma j} \frac{\partial W_{\lambda\sigma}}{\partial b} + \frac{\partial \left(V^a_{\mathrm{NR}}\right)}{\partial b} + \sum_{\mu,\nu} D_{\mu\nu} \frac{\partial W^a_{\mu\nu}}{\partial b} + \frac{1}{2} \sum_{t,s}^{N_{\mathrm{TS}}} \frac{\partial}{\partial b} \left(q_t \frac{\partial C_{ts}}{\partial a} q_s \right) .
\end{aligned} \tag{15}$$

The last three terms can be expanded further

$$\begin{aligned}
\frac{\partial^2 E}{\partial a \partial b} =& \sum_{i}^{\mathrm{occ}} \left[h_{ii}^{ab} + F_{ii}^{ab} + W_{ii}^{ab} - S_{ii}^{ab}\epsilon_i \right] + E_{\mathrm{NR}}^{ab} + \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} 4 S_{ij}^{b} S_{ij}^{a} \epsilon_i + \sum_{t}^{N_{\mathrm{TS}}} \sum_{A} q_t \frac{\partial^2}{\partial a \partial b} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&+ \sum_{m}^{\mathrm{vir}} \sum_{i}^{\mathrm{occ}} U_{mi}^{b} \left[4F_{mi}^{a} + 4W_{mi}^{a} - 4S_{mi}^{a}\epsilon_i - 2\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{a} A_{mi,kl} - 2\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{a} A_{mi,kl}^{\mathrm{PCM}} \right] \\
&- \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} S_{ij}^{b} \left[2F_{ij}^{a} + 2W_{ij}^{a} - \frac{1}{2}\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl} - \frac{1}{2}\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl}^{\mathrm{PCM}} \right] \\
&- \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} S_{ij}^{a} \left[2F_{ij}^{b} + 2W_{ij}^{b} - \frac{1}{2}\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl} - \frac{1}{2}\sum_{k}^{\mathrm{occ}} \sum_{l}^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl}^{\mathrm{PCM}} \right] \\
&+ 2\sum_{i,j}^{\mathrm{occ}} \sum_{t,s}^{N_{\mathrm{TS}}} S_{ij}^{a} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle C_{ts}^{-1} \left[\sum_{A} \left(\frac{Z_A}{|\mathrm{R}_A - \mathrm{R}_s|} \right)^{b} + \sum_{\mu,\nu} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| \nu \right\rangle^{b} \right] \\
&- 4\sum_{m}^{\mathrm{all}} \sum_{i}^{\mathrm{occ}} \sum_{t,s}^{N_{\mathrm{TS}}} U_{mi}^{b} \left\langle m \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| i \right\rangle C_{ts}^{-1} \left[\sum_{A} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right)^{a} + \sum_{\mu,\nu} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R_t}|} \right| \nu \right\rangle^{a} \right] \\
&- \sum_{t,s}^{N_{\mathrm{TS}}} \sum_{A} \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) C_{ts}^{-1} \left[\sum_{\mu,\nu} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| \nu \right\rangle^{b} + \sum_{B} \frac{\partial}{\partial b} \left(\frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_t|} \right) \right] \\
&- \sum_{t,s}^{N_{\mathrm{TS}}} \sum_{\mu,\nu} C_{ts}^{-1} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R_t}|} \right| \nu \right\rangle^{a} \left[\sum_{\lambda,\sigma} D_{\lambda\sigma} \left\langle \lambda \left| \frac{-1}{|\mathbf{r} - \mathbf{R_s}|} \right| \sigma \right\rangle^{b} + \sum_{B} \frac{\partial}{\partial b} \left(\frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_t|} \right) \right] \\
&- \sum_{s,t,u}^{N_{\mathrm{TS}}} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} \left[\frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) + \sum_{\mu,\nu} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathbf{r} - \mathbf{R_t}|} \right| \nu \right\rangle^{a} \right] \\
&+ 2\sum_{i,j}^{\mathrm{occ}} \sum_{s,t,u}^{N_{\mathrm{TS}}} S_{ij}^{a} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle + \frac{1}{2}\sum_{t,s}^{N_{\mathrm{TS}}} \frac{\partial}{\partial b} \left(q_t \frac{\partial C_{ts}}{\partial a} q_s \right).
\end{aligned} \tag{16}$$

Defining

$$V_t^a = \sum_{A} \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) + \sum_{\mu,\nu} D_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| \nu \right\rangle^{a}, \tag{17}$$

Eq. 16 can be converted to

$$
\begin{aligned}
\frac{\partial^2 E}{\partial a \partial b} =& \sum_{i}^{\text{occ}} \left[h_{ii}^{ab} + F_{ii}^{ab} + W_{ii}^{ab} - S_{ii}^{ab}\epsilon_i \right] + E_{\text{NR}}^{ab} + \sum_{i}^{\text{occ}}\sum_{j}^{\text{occ}} 4S_{ij}^{b}S_{ij}^{a}\epsilon_i + \sum_{t}^{N_{\text{TS}}}\sum_{A} q_t \frac{\partial^2}{\partial a \partial b}\left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&+ \sum_{m}^{\text{vir}}\sum_{i}^{\text{occ}} U_{mi}^{b} \left[4F_{mi}^{a} + 4W_{mi}^{a} - 4S_{mi}^{a}\epsilon_i - 2\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{a} A_{mi,kl} \right. \\
&\left. -2\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{a} A_{mi,kl}^{\text{PCM}} - 4\sum_{t,s}^{N_{\text{TS}}} \left\langle m \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_s|} \right| i \right\rangle C_{ts}^{-1} V_s^a \right] - \sum_{t,s}^{N_{\text{TS}}} C_{ts}^{-1} V_t^a V_s^b \\
&- \sum_{i}^{\text{occ}}\sum_{j}^{\text{occ}} S_{ij}^{b} \left[2F_{ij}^{a} + 2W_{ij}^{a} - \frac{1}{2}\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{a} A_{ij,kl} - \frac{1}{2}\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{a} A_{ij,kl}^{\text{PCM}} - 2\sum_{t,s}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle C_{ts}^{-1} V_s^a \right] \\
&- \sum_{i}^{\text{occ}}\sum_{j}^{\text{occ}} S_{ij}^{a} \left[2F_{ij}^{b} + 2W_{ij}^{b} - \frac{1}{2}\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{b} A_{ij,kl} - \frac{1}{2}\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} S_{kl}^{b} A_{ij,kl}^{\text{PCM}} - 2\sum_{t,s}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle C_{ts}^{-1} V_s^b \right] \\
&- \sum_{s,t,u}^{N_{\text{TS}}} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} V_t^a + 2\sum_{i,j}^{\text{occ}}\sum_{s,t,u}^{N_{\text{TS}}} S_{ij}^{a} q_s \frac{\partial C_{su}}{\partial b} C_{ut}^{-1} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle + \frac{1}{2}\sum_{t,s}^{N_{\text{TS}}} \frac{\partial}{\partial b}\left(q_t \frac{\partial C_{ts}}{\partial a} q_s \right). \qquad (18)
\end{aligned}
$$

The remaining term is

$$
\begin{aligned}
\frac{1}{2}\sum_{t,s}^{N_{\text{TS}}} \frac{\partial}{\partial b}\left(q_t \frac{\partial C_{ts}}{\partial a} q_s \right) =& \sum_{t,s}^{N_{\text{TS}}} \frac{\partial q_t}{\partial b}\frac{\partial C_{ts}}{\partial a} q_s + \frac{1}{2}\sum_{t,s}^{N_{\text{TS}}} q_t \frac{\partial^2 C_{ts}}{\partial a \partial b} q_s \\
=& -\sum_{s,t,u}^{N_{\text{TS}}} V_u \frac{\partial C_{ut}^{-1}}{\partial b}\frac{\partial C_{ts}}{\partial a} q_s - \sum_{s,t,u}^{N_{\text{TS}}} V_u^b C_{ut}^{-1}\frac{\partial C_{ts}}{\partial a} q_s \\
&- \sum_{s,t,u}^{N_{\text{TS}}}\sum_{m}^{\text{all}}\sum_{i}^{\text{occ}} 4U_{mi}^{b} \left\langle m \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| i \right\rangle C_{ut}^{-1}\frac{\partial C_{ts}}{\partial a} q_s + \frac{1}{2}\sum_{t,s}^{N_{\text{TS}}} q_t \frac{\partial^2 C_{ts}}{\partial a \partial b} q_s \\
=& -\sum_{s,t,u,v}^{N_{\text{TS}}} q_v \frac{\partial C_{vu}}{\partial b} C_{ut}^{-1}\frac{\partial C_{ts}}{\partial a} q_s - \sum_{s,t,u}^{N_{\text{TS}}} V_u^b C_{ut}^{-1}\frac{\partial C_{ts}}{\partial a} q_s \\
&- \sum_{s,t,u}^{N_{\text{TS}}}\sum_{m}^{\text{all}}\sum_{i}^{\text{occ}} 4U_{mi}^{b} \left\langle m \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| i \right\rangle C_{ut}^{-1}\frac{\partial C_{ts}}{\partial a} q_s + \frac{1}{2}\sum_{t,s}^{N_{\text{TS}}} q_t \frac{\partial^2 C_{ts}}{\partial a \partial b} q_s. \qquad (19)
\end{aligned}
$$

Finally, one obtains

$$
\begin{aligned}
\frac{\partial^2 E}{\partial a \partial b} =& \sum_i^{\mathrm{occ}} \left[h_{ii}^{ab} + F_{ii}^{ab} + W_{ii}^{ab} - S_{ii}^{ab}\epsilon_i \right] + E_{\mathrm{NR}}^{ab} + \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} 4 S_{ij}^{b} S_{ij}^{a} \epsilon_i + \sum_t^{N_{\mathrm{TS}}} \sum_A q_t \frac{\partial^2}{\partial a \partial b} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) \\
&+ \sum_m^{\mathrm{vir}} \sum_i^{\mathrm{occ}} U_{mi}^{b} \left[4F_{mi}^{a} + 4W_{mi}^{a} - 4S_{mi}^{a}\epsilon_i - 2\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{a} A_{mi,kl} - 2\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{a} A_{mi,kl}^{\mathrm{PCM}} \right. \\
&\left. - \sum_{s,t,u}^{N_{\mathrm{TS}}} 4 \left\langle m \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| i \right\rangle C_{ut}^{-1} \frac{\partial C_{ts}}{\partial a} q_s - 4 \sum_{t,s}^{N_{\mathrm{TS}}} \left\langle m \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| i \right\rangle C_{ts}^{-1} V_s^{a} \right] \\
&- \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} S_{ij}^{b} \left[2F_{ij}^{a} + 2W_{ij}^{a} - \frac{1}{2}\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{a} A_{ij,kl} - \frac{1}{2}\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{a} A_{ij,kl}^{\mathrm{PCM}} \right. \\
&\left. - \sum_{s,t,u}^{N_{\mathrm{TS}}} 2 \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C_{ut}^{-1} \frac{\partial C_{ts}}{\partial a} q_s - 2 \sum_{t,s}^{N_{\mathrm{TS}}} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle C_{ts}^{-1} V_s^{a} \right] \\
&- \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} S_{ij}^{a} \left[2F_{ij}^{b} + 2W_{ij}^{b} - \frac{1}{2}\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl} - \frac{1}{2}\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{occ}} S_{kl}^{b} A_{ij,kl}^{\mathrm{PCM}} \right. \\
&\left. -2 \sum_{s,t,u}^{N_{\mathrm{TS}}} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C_{ut}^{-1} \frac{\partial C_{ts}}{\partial b} q_s - 2 \sum_{t,s}^{N_{\mathrm{TS}}} \left\langle i \left| \frac{-1}{|\mathbf{r} - \mathbf{R}_t|} \right| j \right\rangle C_{ts}^{-1} V_s^{b} \right] \\
&- \sum_{t,u}^{N_{\mathrm{TS}}} \left[\sum_v^{N_{\mathrm{TS}}} q_v \frac{\partial C_{vu}}{\partial b} + V_u^{b} \right] C_{ut}^{-1} \left[V_t^{a} + \sum_s^{N_{\mathrm{TS}}} \frac{\partial C_{ts}}{\partial a} q_s \right] + \frac{1}{2} \sum_{t,s}^{N_{\mathrm{TS}}} q_t \frac{\partial^2 C_{ts}}{\partial a \partial b} q_s.
\end{aligned}
\tag{20}
$$

4 CPHF equations

The Fock matrix is

$$
\tilde{F}_{ij} = h_{ij} + \sum_k^{\mathrm{occ}} \{2(ij|kk) - (ik|jk)\} + W_{ij} \tag{21}
$$

$$
W_{ij} = \sum_t^{N_{\mathrm{TS}}} \left\langle i \left| \frac{-q_t}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle. \tag{22}
$$

Therefore, the derivative of the Fock matrix is

$$
\frac{\partial \tilde{F}_{ij}}{\partial a} = \sum_m^{\mathrm{all}} U_{mi}^{a} F_{jm} + \sum_m^{\mathrm{all}} U_{mj}^{a} F_{im} + F_{ij}^{a} + \sum_m^{\mathrm{all}} \sum_l^{\mathrm{occ}} U_{ml}^{a} A_{ij,ml} + \frac{\partial W_{ij}}{\partial a} \tag{23}
$$

$$
\frac{\partial W_{ij}}{\partial a} = \sum_m^{\mathrm{all}} U_{mi}^{a} W_{jm} + \sum_m^{\mathrm{all}} U_{mj}^{a} W_{im} + \sum_t^{N_{\mathrm{TS}}} \left\langle i \left| \frac{-q_t}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle^{a} + \sum_t^{N_{\mathrm{TS}}} \frac{\partial q_t}{\partial a} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle. \tag{24}
$$

Eq. 24 can be expanded to

$$\begin{aligned}
\frac{\partial W_{ij}}{\partial a} &= \sum_m^{\text{all}} U^a_{mi} W_{jm} + \sum_m^{\text{all}} U^a_{mj} W_{im} + \sum_t^{N_{\text{TS}}} \left\langle i \left| \frac{-q_t}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle^a \\
&- \sum_t^{N_{\text{TS}}} \sum_I^{N} \frac{\partial}{\partial a} \left(\mathbf{C}^{-1}\mathbf{V}^I\right)_t \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle \\
&= \sum_m^{\text{all}} U^{a,X}_{mi} W^X_{jm} + \sum_m^{\text{all}} U^{a,X}_{mj} W^X_{im} + \sum_t^{N_{\text{TS}}} \left\langle i \left| \frac{-q_t}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle^a \\
&- \sum_t^{N_{\text{TS}}} \sum_I^{N} \left(\mathbf{C}^{-1} \frac{\partial \mathbf{V}^I}{\partial a}\right)_t \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle - \sum_{s,t,u}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C^{-1}_{ut} \frac{\partial C_{ts}}{\partial a} q_s. \qquad (25)
\end{aligned}$$

Therefore,

$$\begin{aligned}
\frac{\partial W_{ij}}{\partial a} &= \sum_m^{\text{all}} U^a_{mi} W_{jm} + \sum_m^{\text{all}} U^a_{mj} W_{im} + \sum_t^{N_{\text{TS}}} \left\langle i \left| \frac{-q_t}{|\mathrm{r} - \mathrm{R}_t|} \right| j \right\rangle^a \\
&+ \sum_t^{N_{\text{TS}}} \frac{\partial V_t}{\partial a} q^{ij}_t - \sum_{s,t,u}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C^{-1}_{ut} \frac{\partial C_{ts}}{\partial a} q_s \qquad (26)
\end{aligned}$$

$$q^{ij}_t = -\sum_s^{N_{\text{TS}}} \left(\mathbf{C}^{-1}\right)_{ts} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_s|} \right| j \right\rangle \qquad (27)$$

$$\frac{\partial V_t}{\partial a} = \sum_A \frac{\partial}{\partial a} \left(\frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_t|} \right) + \sum_{\mu,\nu} D^I_{\mu\nu} \left\langle \mu \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| \nu \right\rangle^a + \sum_k^{\text{all}} \sum_l^{\text{occ}} 4U^{a,I}_{kl} \left\langle k \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| l \right\rangle. \qquad (28)$$

Eq. 23 can be converted to

$$\begin{aligned}
\frac{\partial \tilde{F}_{ij}}{\partial a} &= \sum_m^{\text{all}} U^a_{mi} \tilde{F}_{jm} + \sum_m^{\text{all}} U^a_{mj} \tilde{F}_{im} + \tilde{F}^a_{ij} + \sum_m^{\text{all}} \sum_l^{\text{occ}} U^a_{ml} A_{ij,ml} \\
&+ \sum_t^{N_{\text{TS}}} V^a_t q^{ij}_t - \sum_{s,t,u}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C^{-1}_{ut} \frac{\partial C_{ts}}{\partial a} q_s + \sum_t^{N_{\text{TS}}} \sum_k^{\text{all}} \sum_l^{\text{occ}} 4U^a_{kl} \left\langle k \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| l \right\rangle q^{ij}_t \qquad (29)
\end{aligned}$$

Using the relationship $\partial F_{ij}/\partial a = 0$, CPHF equations are obtained:

$$\begin{aligned}
&-U^a_{ij} \left(\epsilon_i - \epsilon_j\right) - \sum_m^{\text{vir}} \sum_l^{\text{occ}} U^a_{ml} A_{ij,ml} - \sum_t^{N_{\text{TS}}} \sum_k^{\text{vir}} \sum_l^{\text{occ}} 4U^{a,I}_{kl} \left\langle k \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| l \right\rangle q^{ij}_t \\
&= - S^a_{ij} \epsilon^X_j + \tilde{F}^a_{ij} - \frac{1}{2} \sum_k^{\text{all}} \sum_l^{\text{occ}} S^a_{kl} A_{ij,kl} + \sum_t^{N_{\text{TS}}} \sum_k^{\text{occ}} \sum_l^{\text{occ}} 2S^a_{kl} \left\langle k \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_t|} \right| l \right\rangle q^{ij}_t \\
&- \sum_{s,t,u}^{N_{\text{TS}}} \left\langle i \left| \frac{-1}{|\mathrm{r} - \mathrm{R}_u|} \right| j \right\rangle C^{-1}_{ut} \frac{\partial C_{ts}}{\partial a} q_s + \sum_t^{N_{\text{TS}}} V^a_t q^{ij}_t \qquad (30)
\end{aligned}$$

5 Raman spectra for polyalanine

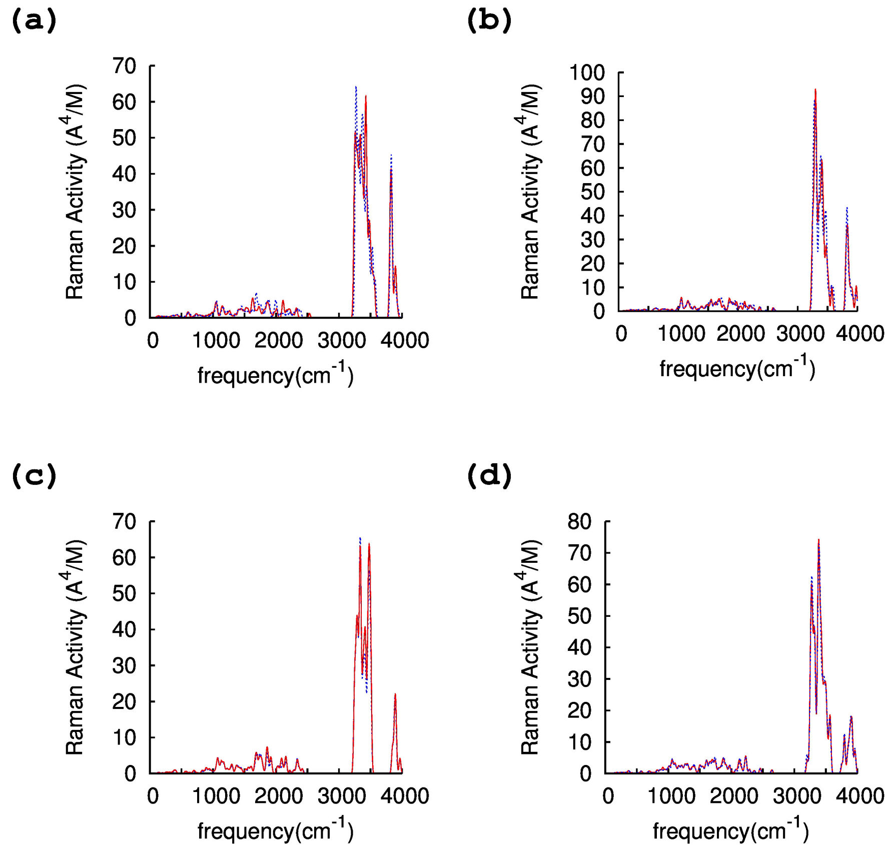

Figure 1: Raman spectra for the α-helices and extended (e) forms of dekapeptides (a) $\alpha(\text{Ala})_{10}$, (b) $\text{e}(\text{Ala})_{10}$, (c) $\alpha(\text{Ala})_9(\text{Arg})$, (d) $\text{e}(\text{Ala})_9(\text{Arg})$. FMO-PCM$\langle 1 \rangle$ and full unfragmented results are shown with red solid and blue dashed lines, respectively.

Table 1: Comparison of FMO-RHF/PCM and full RHF/PCM Raman peaks.

method	FMO2		full	
	frequency	intensity	frequency	intensity
		α(Ala)$_{10}$		
peak1	1631	5.528	1686	7.041
peak2	1865	4.458	1884	5.141
peak3	3259	51.767	3272	64.012
peak4	3339	50.821	3374	56.421
peak5	3427	61.370	3437	36.545
peak6	3826	41.375	3830	45.227
		e(Ala)$_{10}$		
peak1	1688	5.860	1698	5.669
peak2	1861	7.381	1861	5.583
peak3	3288	43.831	3288	43.857
peak4	3338	63.116	3338	65.521
peak5	3480	63.585	3479	56.445
peak6	3895	22.032	3892	21.600
		α(Ala)$_9$(Arg)		
peak1	1053	5.748	1050	4.788
peak2	1162	4.477	1175	4.027
peak3	1552	4.913	1532	4.291
peak4	1685	5.263	1618	4.170
peak5	1858	5.341	1865	4.125
peak6	3301	92.833	3282	87.988
peak7	3406	63.266	3390	64.876
peak8	3835	36.407	3828	43.274
		e(Ala)$_9$(Arg)		
peak1	1698	4.465	1744	5.274
peak2	1874	4.865	1882	5.263
peak3	3318	46.630	3278	62.603
peak4	3388	74.148	3392	72.697
peak5	3795	11.658	3796	12.646

6 IR spectra for ionic liquid

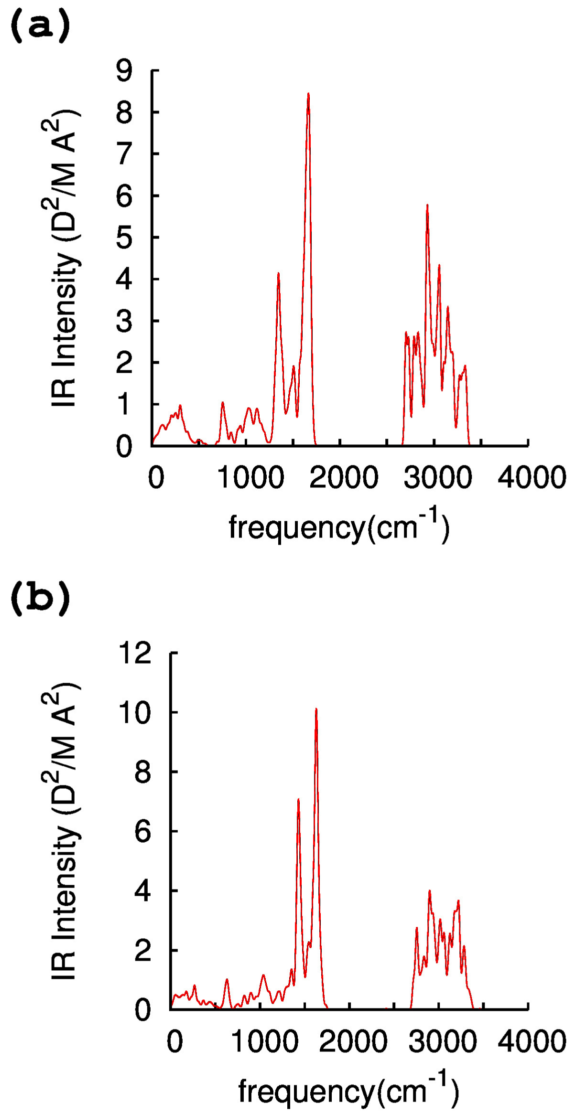

Figure 2: IR spectra for (a) DMEDAH, and (b) DMPDAH. The frequencies are scaled by 0.8953.

References

[1] M. Cossi and V. Barone, J. Chem. Phys. **109**, 6246 (1998).

7 Detailed accuracy of vibrational frequencies

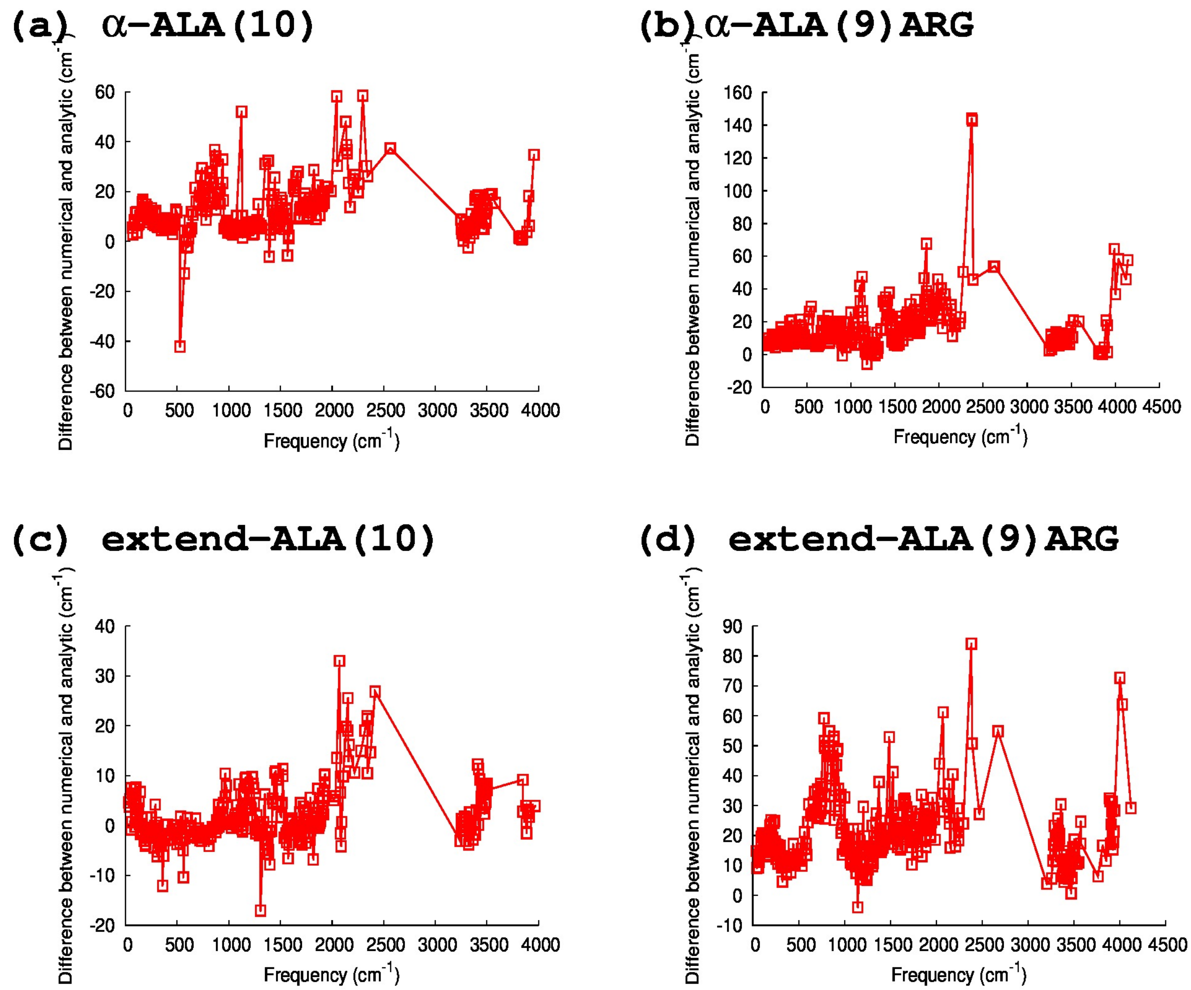

Figure 3: Differences of vibrational frequenies obtained with numerical and analytic FMO Hessians. (a) α-(ala)10 (b) α-arg (ala)9 (c) β-(ala)10 (d) β-arg (ala)9

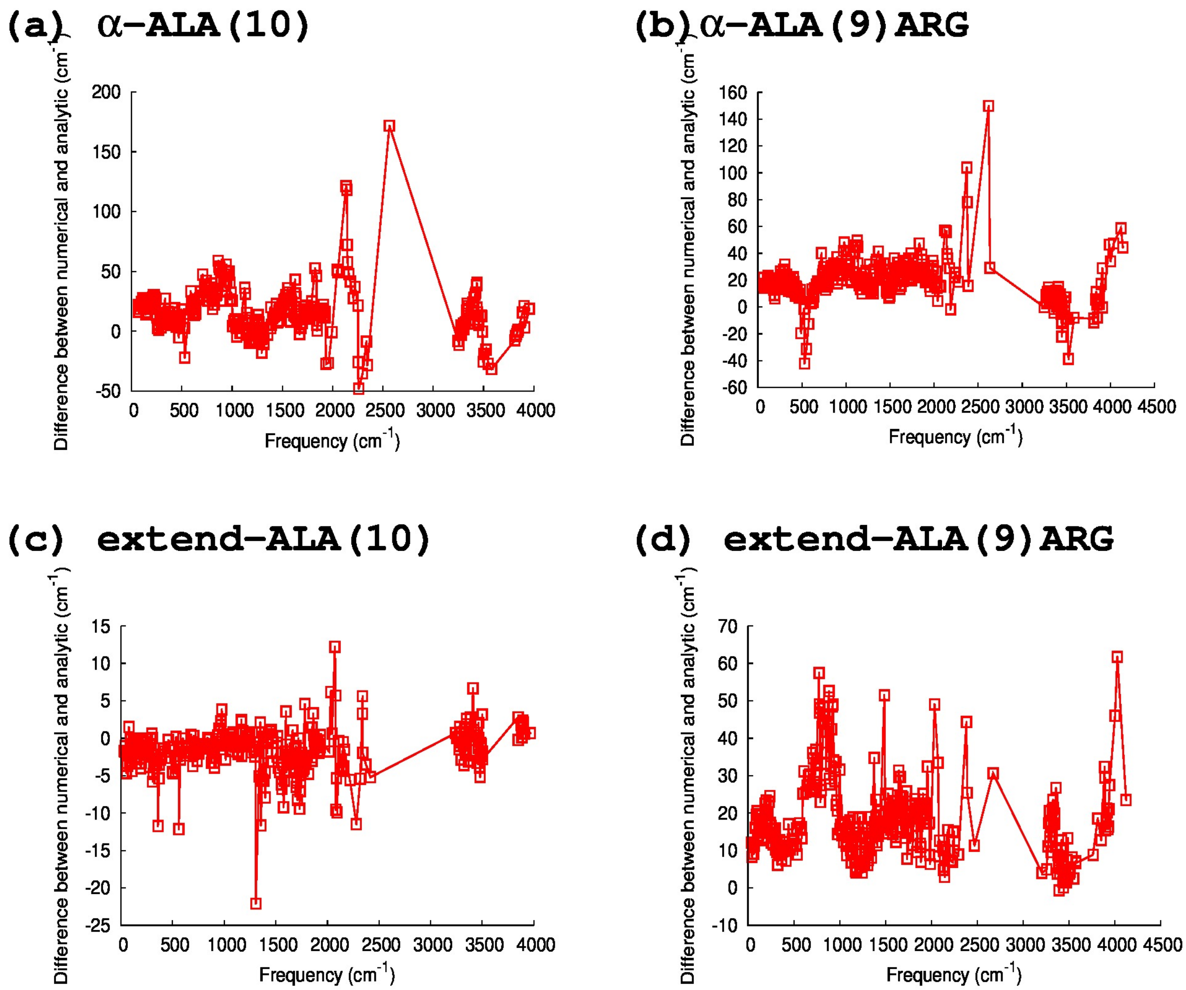

Figure 4: Differences of vibrational frequenies obtained with analytic Hessian without fragmentation and analytic FMO Hessians. (a) α-(ala)10 (b) α-arg (ala)9 (c) β-(ala)10 (d) β-arg (ala)9