Bond Detectors for Molecular Dynamics Simulations: Hydrogen Bond

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OUTLINES

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MODEL SYSTEMS

COMPUTATIONAL DETAILS

RESULTS

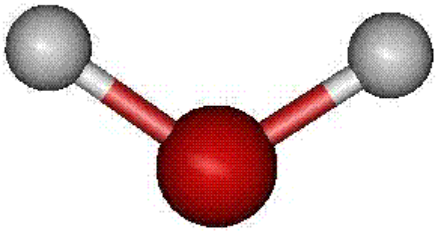
- Charge Reorganization
- Fukui Function Profiles
- Polarization Profiles
- Hardness Profile

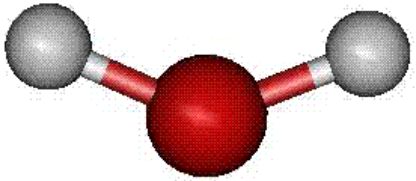
CONCLUSIONS

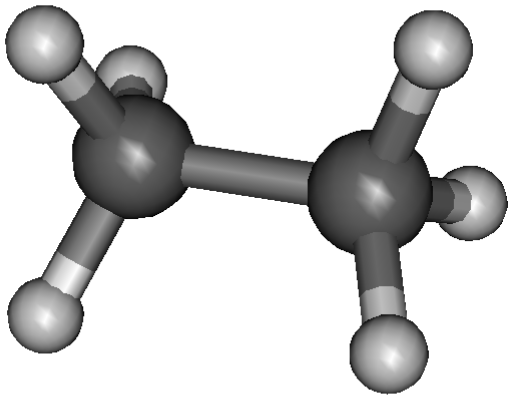
Molecular Dynamics Simulations

$$E_{pot} = \sum_i k_{R_i}\left(R_i - R_i^0\right)^2 + \sum_i k_{\vartheta_i}\left(\vartheta_i - \vartheta_i^0\right)^2 + \sum_i \frac{V_{n_i}}{2}\left[1 + \cos\left(n_i\varphi_i - \varphi_i^0\right)\right]$$

$$+ \sum_{i<j} \varepsilon_{ij}\left[\left(\frac{r_{ij}^*}{r_{ij}}\right)^{12} - 2\left(\frac{r_{ij}^*}{r_{ij}}\right)^{6}\right] \qquad + \sum_{i<j} \frac{q_i q_j}{\varepsilon\, r_{ij}}$$



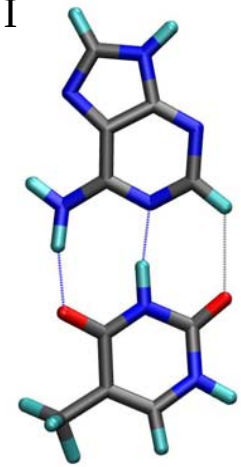




Model Systems

Model Systems

I



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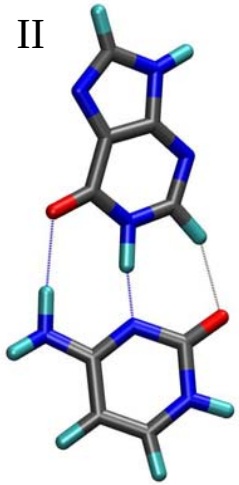

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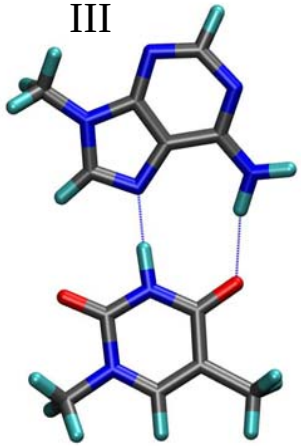

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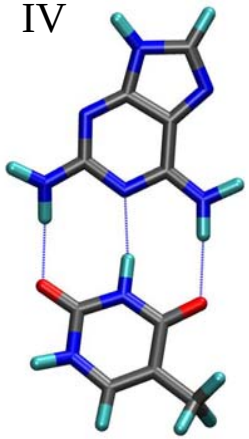

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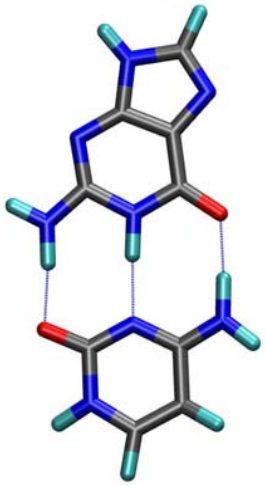
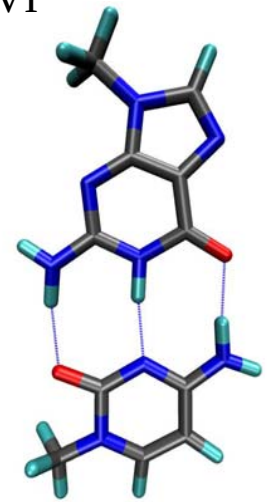


VI



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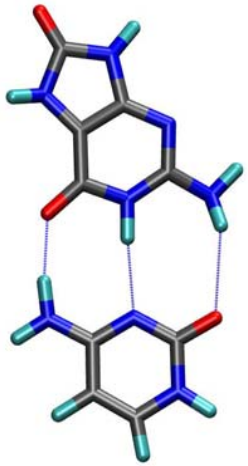
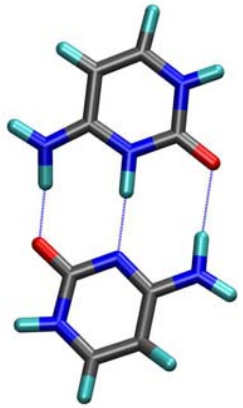


VIII



Hydrogen bonded base pairs. Structures I-VIII correspond to A-T, H-C, mA-mT, aA-T, G-C, mG-mC, 8oG-C, and C-C, respectively. Abreviation used: A=adenine, C=cytosine, G=guanine, H=hypoxantine, T=thymine, m=methyl, and a=amino.

Computational Details

Born-Oppenheimer Molecular Dynamics (MD) simulations –TERACHEM package
Molecular Dynamics Simulations - NAMD2 package
force field – AMBER99ff
initial geometries - B3LYP/6-31G(d) level of theory
charge distribution – Mulliken charges
time step – 1 fs
time – 10 ps

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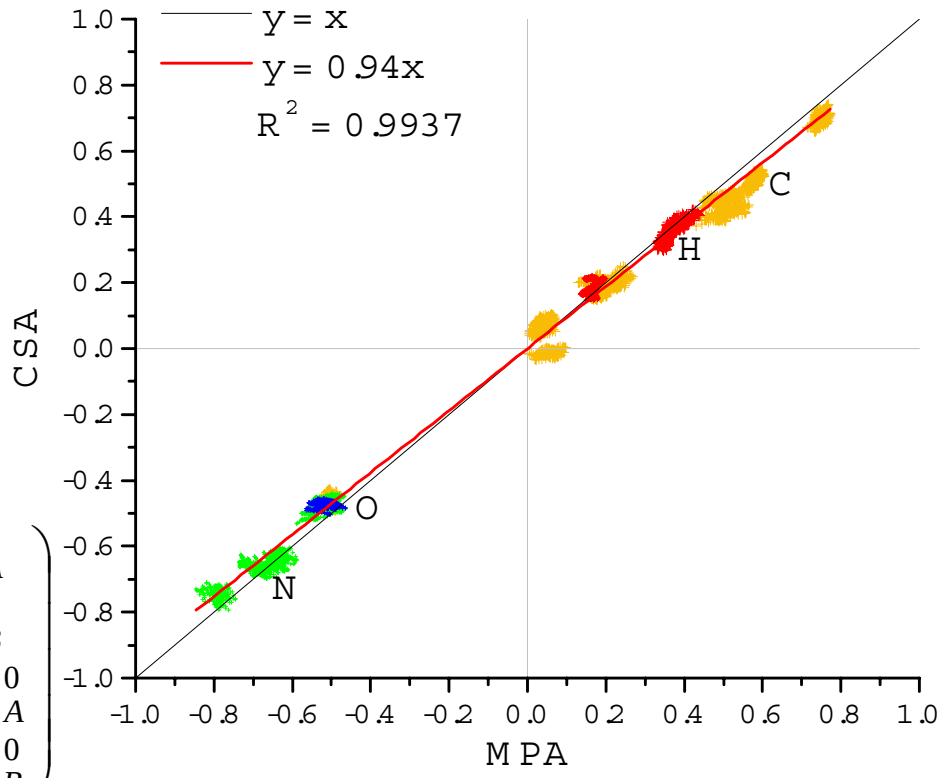
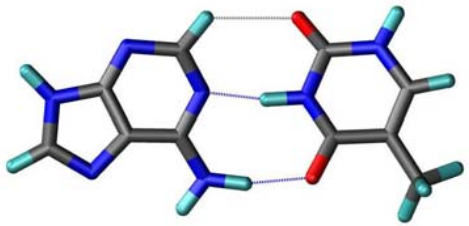
Charge Reorganization

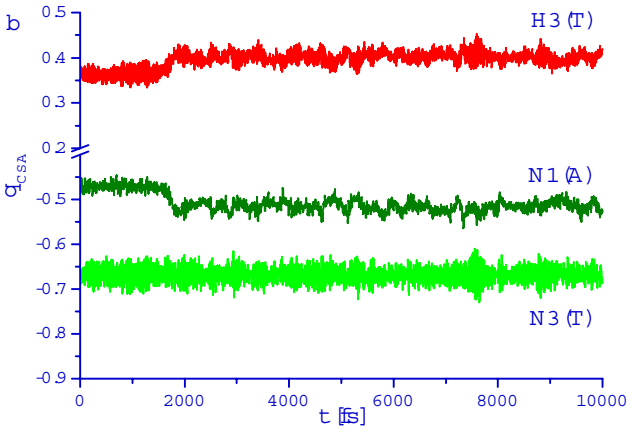
$$\begin{pmatrix} 0 & 0 & \mathbf{1}_A & \mathbf{0}_B \\ 0 & 0 & \mathbf{0}_A & \mathbf{1}_B \\ \mathbf{1}_A^{\dagger} & \mathbf{0}_A^{\dagger} & \boldsymbol{\eta}_{AA}^{0} & \boldsymbol{\eta}_{AB}^{0} \\ \mathbf{0}_B^{\dagger} & \mathbf{1}_B^{\dagger} & \boldsymbol{\eta}_{BA}^{0} & \boldsymbol{\eta}_{BB}^{0} \end{pmatrix} \begin{pmatrix} -\chi_A^{eq} \\ -\chi_B^{eq} \\ \boldsymbol{q}_A \\ \boldsymbol{q}_B \end{pmatrix} = \begin{pmatrix} q_A \\ q_B \\ -\chi_A^{0} \\ -\chi_B^{0} \end{pmatrix}$$

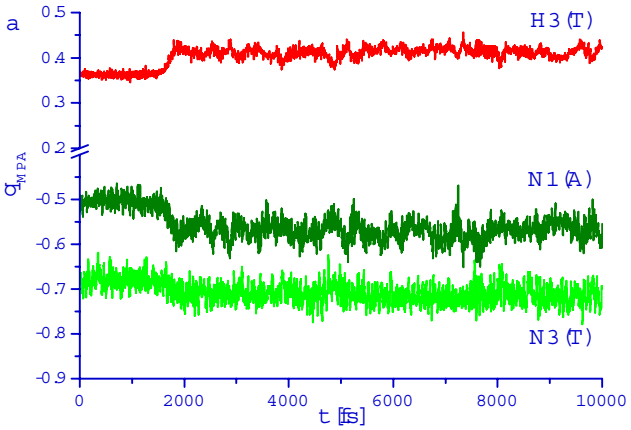
$$\begin{pmatrix} -\chi_A^{eq} \\ -\chi_B^{eq} \\ \boldsymbol{q}_A \\ \boldsymbol{q}_B \end{pmatrix} = \begin{pmatrix} -\eta_{AA} & -\eta_{AB} & \boldsymbol{f}_{AA} & \boldsymbol{f}_{AB} \\ -\eta_{BA} & -\eta_{BB} & \boldsymbol{f}_{BA} & \boldsymbol{f}_{BB} \\ \boldsymbol{f}_{AA}^{\dagger} & \boldsymbol{f}_{AB}^{\dagger} & -\boldsymbol{\beta}_{AA} & -\boldsymbol{\beta}_{AB} \\ \boldsymbol{f}_{BA}^{\dagger} & \boldsymbol{f}_{BB}^{\dagger} & -\boldsymbol{\beta}_{BA} & -\boldsymbol{\beta}_{BB} \end{pmatrix} \begin{pmatrix} q_A \\ q_B \\ -\chi_A^{0} \\ -\chi_B^{0} \end{pmatrix}$$

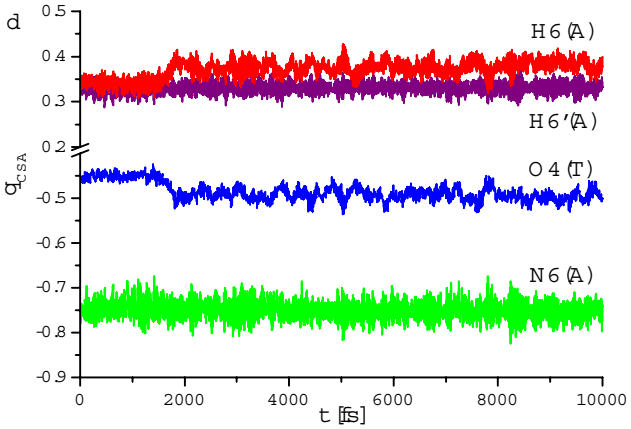


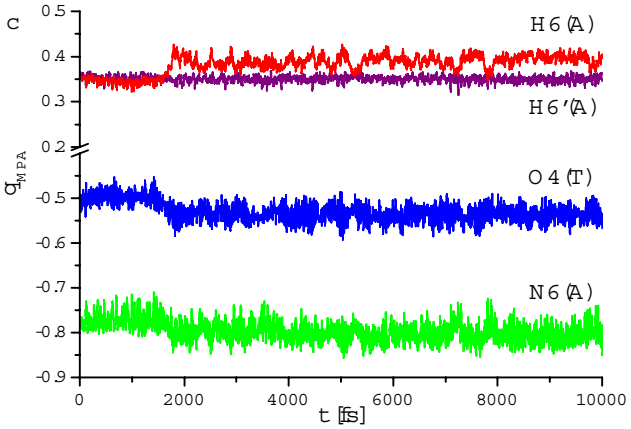


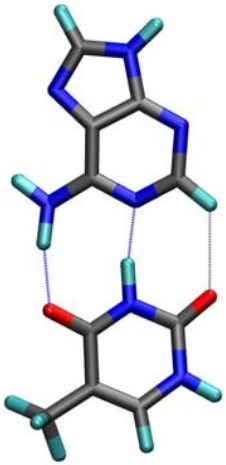
Charge Reorganization



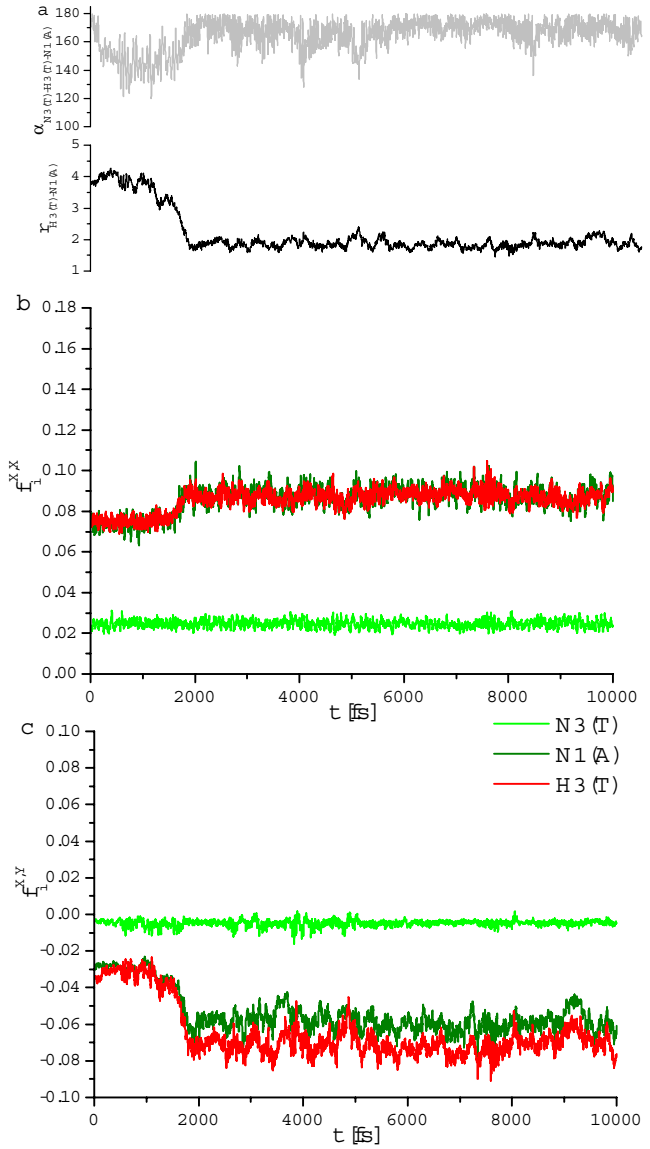








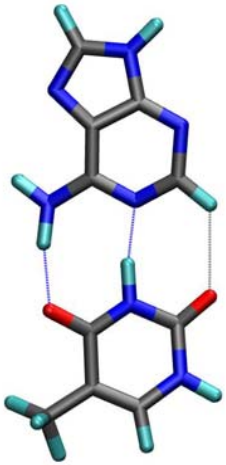
Fukui Function Profiles



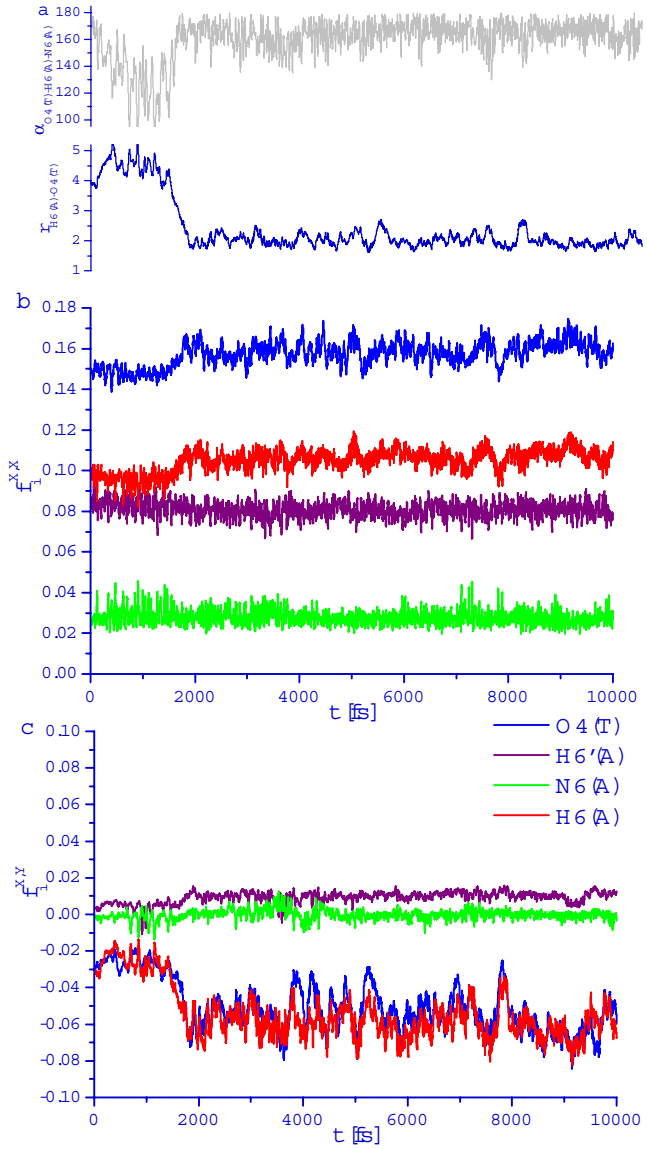
$$E = E[N_{M_1}, N_{M_2}, ..., N_{M_n}, v_{M_1}(\vec{r}), v_{M_2}(\vec{r}), ..., v_{M_n}(\vec{r})]$$

$$f_{M_i,M_j}(\vec{r}) = \left(\delta\mu_{M_j} / \delta v_{M_i}(\vec{r})\right)_{N,\{v_{M_k}, k\neq i\}}$$
$$= \left(\partial\rho_{M_i}(\vec{r}) / \partial N_{M_j}\right)_{v(\vec{r}),\{N_{M_k}, k\neq j\}}$$

$$\boldsymbol{f}_{M_i,M_j} = \left(\partial \boldsymbol{N}_{M_i} / \partial N_{M_j}\right)_{\boldsymbol{v},\{N_k, k\neq j\}}$$



Fukui Function Profiles



$$E = E[N_{M_1}, N_{M_2}, ..., N_{M_n}, v_{M_1}(\vec{r}), v_{M_2}(\vec{r}), ..., v_{M_n}(\vec{r})]$$

$$f_{M_i,M_j}(\vec{r}) = \left(\delta\mu_{M_j} / \delta v_{M_i}(\vec{r})\right)_{N,\{v_{M_k}, k\neq i\}}$$
$$= \left(\partial\rho_{M_i}(\vec{r}) / \partial N_{M_j}\right)_{v(\vec{r}),\{N_{M_k}, k\neq j\}}$$

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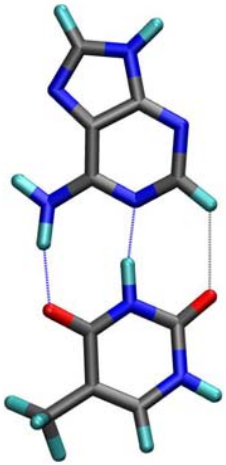
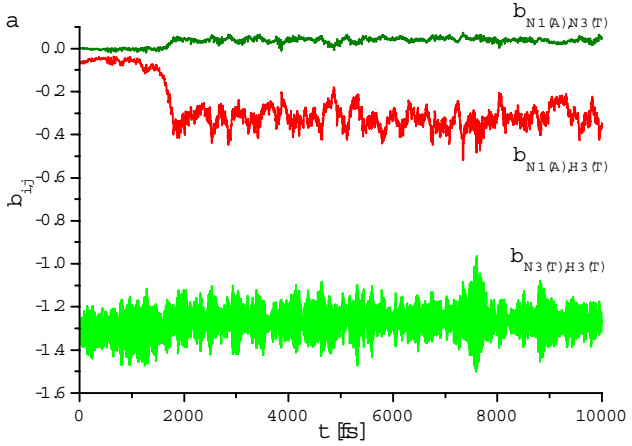
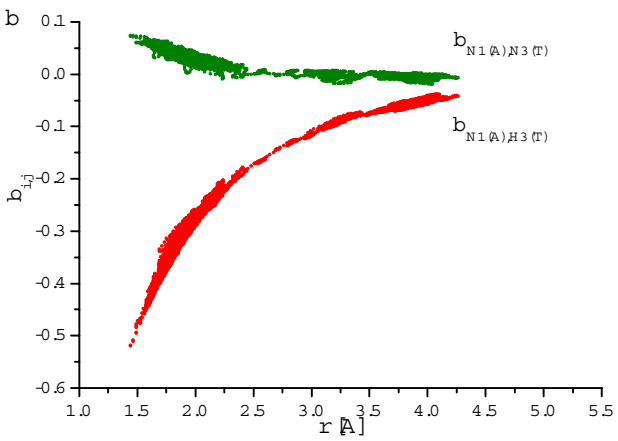
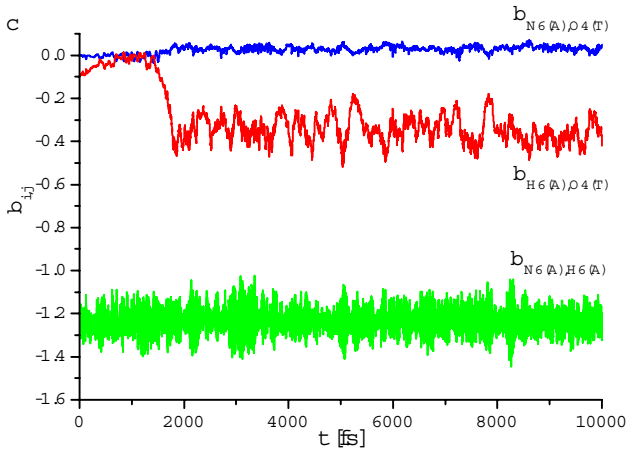


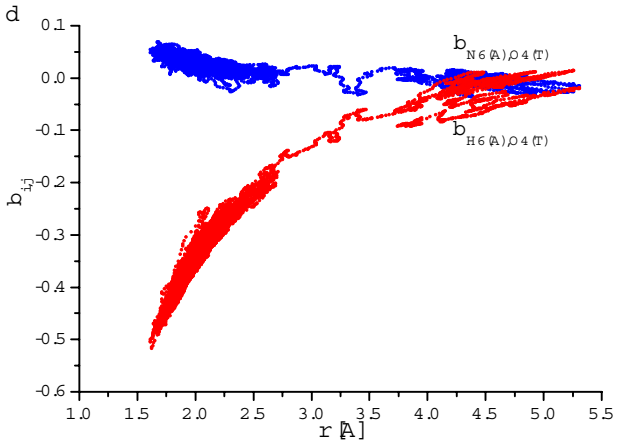
Polarization Profiles

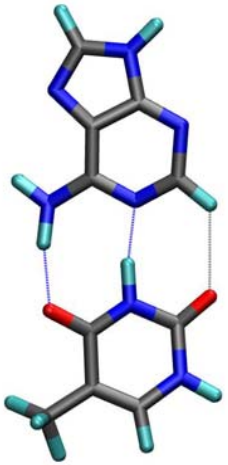
$$\boldsymbol{\beta}_{M_i,M_j} = \left(\partial \mathbf{N}_{M_i} / \delta \mathbf{v}_{M_j}\right)_{N,\{\mathbf{v}_{M_k},\, k\neq j\}} = \left(\partial \mathbf{N}_{M_j} / \delta \mathbf{v}_{M_i}\right)_{N,\{\mathbf{v}_{M_k},\, k\neq i\}}$$





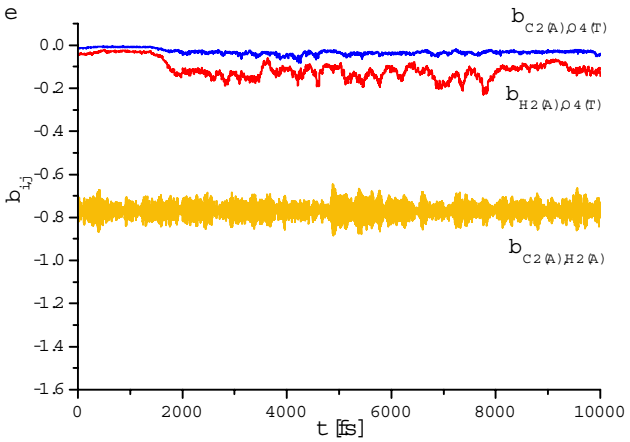


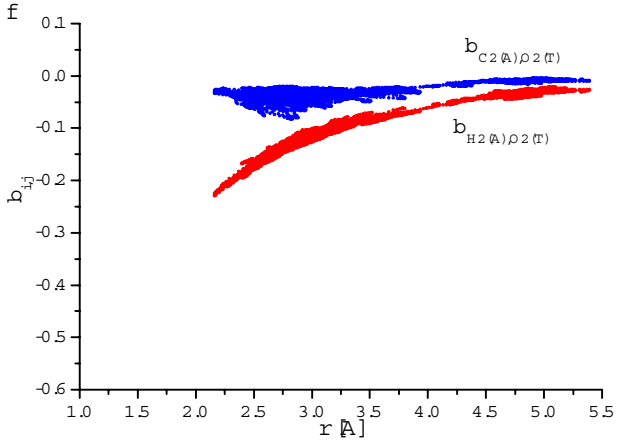


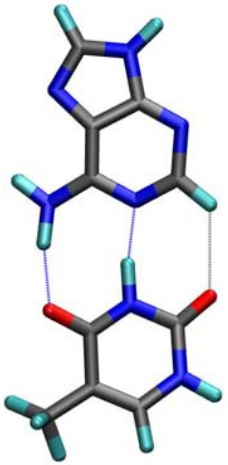


Polarization Profiles

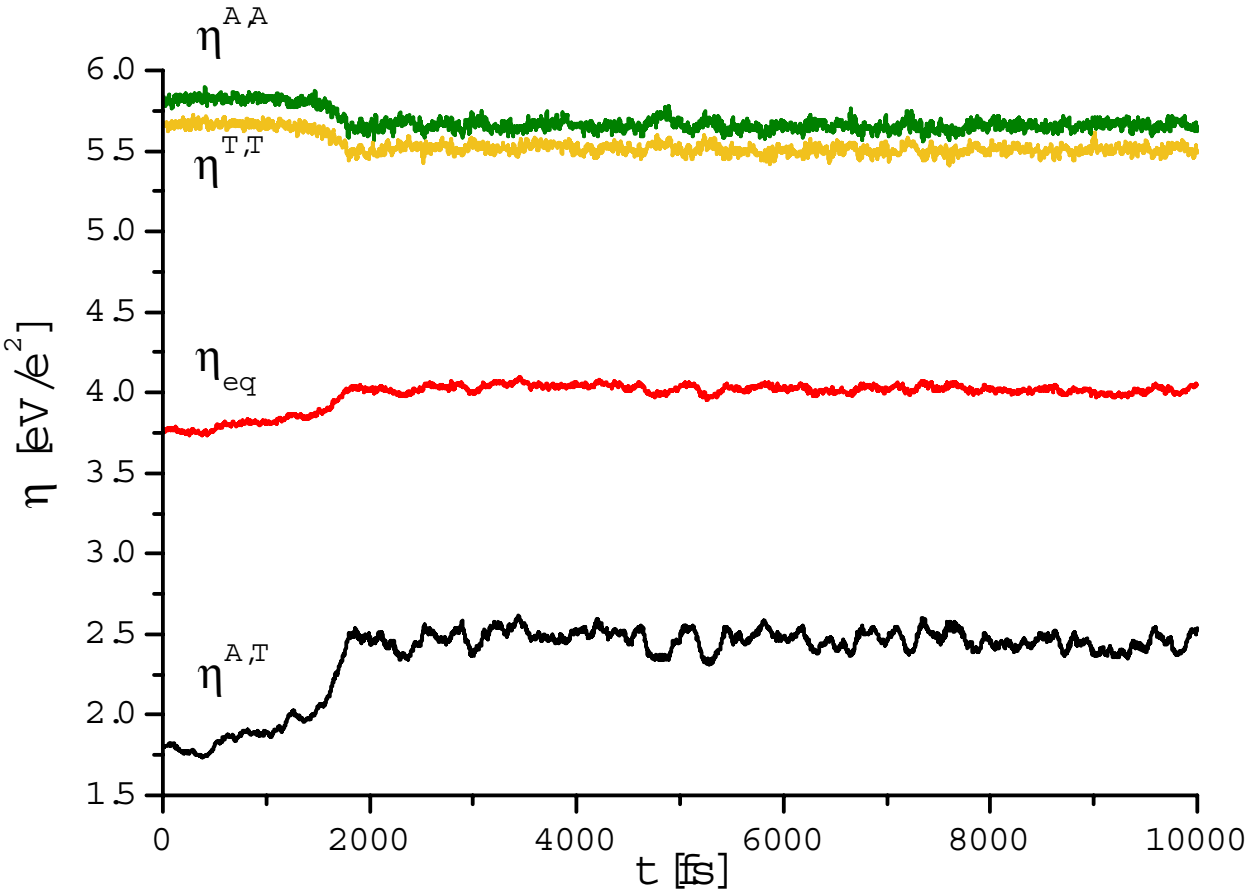
$$\boldsymbol{\beta}_{M_i,M_j} = \left(\partial \mathbf{N}_{M_i} / \delta \mathbf{v}_{M_j}\right)_{N,\{\mathbf{v}_{M_k},\, k\neq j\}} = \left(\partial \mathbf{N}_{M_j} / \delta \mathbf{v}_{M_i}\right)_{N,\{\mathbf{v}_{M_k},\, k\neq i\}}$$







Hardness Profiles



$$\eta_{M_i,M_j} = \left(\partial^2 E / \partial N_{M_i} \partial N_{M_j}\right)_{v(\vec{r})} = \left(\partial \mu_{M_i} / \partial N_{M_j}\right)_{v(\vec{r})} = \left(\partial \mu_{M_j} / \partial N_{M_i}\right)_{v(\vec{r})}$$

$$\eta = \left(\partial^2 E / \partial N^2\right)_{v(\vec{r})} = \left(\partial \mu / \partial N\right)_{v(\vec{r})} = -\left(\partial \chi / \partial N\right)_{v(\vec{r})}$$

Conclusions

- CSA formalism correctly reproduced charge reorganization accompanying hydrogen bond formation.
- Fukui function indices and polarization matrix elements are good bond detectors.

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CSA calculations: computer cluster purchased with the financial support from the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (Contract No. POIG.02.01.00-12-023/08).

TeraChem calculations: ACK CYFRONET.