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

Supporting information for

Computational Modeling of Self-Trapped Electrons in Rutile TiO_2

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S1. The Hamiltonian and overlap matrices for the electron polaron that consists of a titanium-centered pivotal complex and all of its nearest neighbors. All numbers in the Hamiltonian matrices are in units of eV.

$$H = \begin{pmatrix}
0 & -71.0603 & -71.0603 & -0.5078 & -0.5078 & -0.5078 & -0.5078 & -0.5078 & -0.5078 & -0.5078 & -0.5078 \\
-71.0603 & 6.9423 & 0 & -0.5078 & 0 & -0.5078 & 0 & -0.5078 & 0 & -0.5078 & 0 \\
-71.0603 & 0 & 6.9423 & 0 & -0.5078 & 0 & -0.5078 & 0 & -0.5078 & 0 & -0.5078 \\
-0.5078 & -0.5078 & 0 & 6.5090 & -71.0603 & 0 & 0 & 0 & 0 & 0 & 0 \\
-0.5078 & 0 & -0.5078 & -71.0603 & 6.5090 & 0 & 0 & 0 & 0 & 0 & 0 \\
-0.5078 & -0.5078 & 0 & 0 & 0 & 6.5090 & -71.0603 & 0 & 0 & 0 & 0 \\
-0.5078 & 0 & -0.5078 & 0 & 0 & -71.0603 & 6.5090 & 0 & 0 & 0 & 0 \\
-0.5078 & -0.5078 & 0 & 0 & 0 & 0 & 0 & 6.5090 & -71.0603 & 0 & 0 \\
-0.5078 & 0 & -0.5078 & 0 & 0 & 0 & 0 & -71.0603 & 6.5090 & 0 & 0 \\
-0.5078 & -0.5078 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6.5090 & -71.0603 \\
-0.5078 & 0 & -0.5078 & 0 & 0 & 0 & 0 & 0 & 0 & -71.0603 & 6.5090
\end{pmatrix}$$

$$S = \begin{pmatrix}
1 & 0.7611 & 0.7611 & 0.0147 & 0.0147 & 0.0147 & 0.0147 & 0.0147 & 0.0147 & 0.0147 & 0.0147 \\
0.7611 & 1 & 0 & 0.0147 & 0 & 0.0147 & 0 & 0.0147 & 0 & 0.0147 & 0 \\
0.7611 & 0 & 1 & 0 & 0.0147 & 0 & 0.0147 & 0 & 0.0147 & 0 & 0.0147 \\
0.0147 & 0.0147 & 0 & 1 & 0.7611 & 0 & 0 & 0 & 0 & 0 & 0 \\
0.0147 & 0 & 0.0147 & 0.7611 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0.0147 & 0.0147 & 0 & 0 & 0 & 1 & 0.7611 & 0 & 0 & 0 & 0 \\
0.0147 & 0 & 0.0147 & 0 & 0 & 0.7611 & 1 & 0 & 0 & 0 & 0 \\
0.0147 & 0.0147 & 0 & 0 & 0 & 0 & 0 & 1 & 0.7611 & 0 & 0 \\
0.0147 & 0 & 0.0147 & 0 & 0 & 0 & 0 & 0.7611 & 1 & 0 & 0 \\
0.0147 & 0.0147 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0.7611 \\
0.0147 & 0 & 0.0147 & 0 & 0 & 0 & 0 & 0 & 0 & 0.7611 & 1
\end{pmatrix}$$

S2. The Hamiltonian and overlap matrices for the electron polarons in RT1, RT2, RT3, RT4, and RT5 systesm. All numbers in the Hamiltonian matrices are in units of eV.

$$H = \begin{pmatrix} 0 & -71.0603 & -71.0603 \\ -71.0603 & 6.9423 & 0 \\ -71.0603 & 0 & 6.9423 \end{pmatrix} \qquad S = \begin{pmatrix} 1 & 0.7611 & 0.7611 \\ 0.7611 & 1 & 0 \\ 0.7611 & 0 & 1 \end{pmatrix}$$

(a) RT1

$$H = \begin{pmatrix} 0 & -71.0603 & -71.0603 & 0 & 0 \\ -71.0603 & 6.9423 & 0 & -71.0603 & 0 \\ -71.0603 & 0 & 6.9423 & 0 & -71.0603 \\ 0 & -71.0603 & 0 & 6.6275 & 0 \\ 0 & 0 & -71.0603 & 0 & 6.6275 \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & 0.7611 & 0.7611 & 0 & 0 \\ 0.7611 & 1 & 0 & 0.7611 & 0 \\ 0.7611 & 0 & 1 & 0 & 0.7611 \\ 0 & 0.7611 & 0 & 1 & 0 \\ 0 & 0 & 0.7611 & 0 & 1 \end{pmatrix}$$

(b) RT2

$$H = \begin{pmatrix} 0 & -71.0603 & -71.0603 & 0 & 0 & 0 & 0 \\ -71.0603 & 6.9423 & 0 & -71.0603 & 0 & 0 & 0 \\ -71.0603 & 0 & 6.9423 & 0 & -71.0603 & 0 & 0 \\ 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 & 0 \\ 0 & 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 \\ 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 \\ 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & 0.7611 & 0.7611 & 0 & 0 & 0 & 0 \\ 0.7611 & 1 & 0 & 0.7611 & 0 & 0 & 0 \\ 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 \\ 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 \\ 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 \\ 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 \end{pmatrix}$$

(c) RT3

$$H = \begin{pmatrix} 0 & -71.0603 & -71.0603 & 0 & 0 & 0 & 0 & 0 & 0 \\ -71.0603 & 6.9423 & 0 & -71.0603 & 0 & 0 & 0 & 0 & 0 \\ -71.0603 & 0 & 6.9423 & 0 & -71.0603 & 0 & 0 & 0 & 0 \\ 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 & 0 & 0 & 0 \\ 0 & 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 & 0 & 0 \\ 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 & 0 \\ 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 \\ 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & 0.7611 & 0.7611 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.7611 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 & 0 \\ 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 \\ 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 \\ 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 \\ 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 \\ 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 \\ 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 \end{pmatrix}$$

(d) RT4

$$H = \begin{pmatrix} 0 & -71.0603 & -71.0603 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -71.0603 & 6.9423 & 0 & -71.0603 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -71.0603 & 0 & 6.9423 & 0 & -71.0603 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -71.0603 & 0 & 6.6275 & 0 & -71.0603 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 & -71.0603 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -71.0603 & 0 & 6.4295 \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & 0.7611 & 0.7611 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.7611 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 & 0.7611 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.7611 & 0 & 1 \end{pmatrix}$$

(e) RT5

S3. The variance of calculated polaron activation energy, ΔG^*, in system RT5 upon the change of on-site Hubbard potential, U.

U (eV)	1.5	2.5	3.5
ΔG^* (eV)	0.029	0.031	0.034

S4. The variance of calculated isotropic A-tensor, A_{iso}, in system RT5 upon the change of on-site Hubbard potential, U.

U (eV)	1.5	2.5	3.5
$A_{iso}\left(type\ 1\ ^{17}\mathrm{O}\right)$	4.02	5.78	6.82
$A_{iso}\left(type\ 2\ ^{17}\mathrm{O}\right)$	0.96	1.67	2.36