

# Electronic Supplementary Information: Direct Simulation of Electron Transfer in the Cobalt Hexammine(II/III) Self-Exchange Reaction

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## I. Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> Optimization for Partial Charges

As described in the text, Mulliken analysis from gas phase density functional theory is used to assign partial charges to the atoms of the TMC for the atomistic simulations. Using the Gaussian 09<sup>1</sup> software package, the complex is optimized using the M06 hybrid functional<sup>2</sup> with the 6-31G(d,p) basis set<sup>3</sup> for N and H atoms and the LANL2DZ<sup>4</sup> basis set for Co.

The resulting optimized structure is provided in Table S1. The computed energy at this configuration is -483.282740937 hartrees. Partial charges on H atoms from the Mulliken analysis were summed into the N to which they are bonded, and those net partial charges are averaged over each of the N atoms in order to achieve a total charge of +3  $e$  on  $\text{Co}(\text{NH}_3)_6^{3+}$ . The resulting partial charges used in the simulation are +0.41281  $e$  on Co and +0.43119  $e$  on N.

**Table S1:** Optimized  $\text{Co}(\text{NH}_3)_6^{3+}$  geometry

| atom type | $x$       | $y$       | $z$       |
|-----------|-----------|-----------|-----------|
| Co        | 0.000192  | 0.000106  | -0.000008 |
| N         | 1.275211  | -0.743840 | 1.357761  |
| N         | -1.280279 | 0.657544  | -1.397605 |
| N         | 1.159948  | 1.624901  | -0.193382 |
| N         | -1.035952 | 0.985046  | 1.406268  |
| N         | -1.150609 | -1.617457 | 0.288628  |
| N         | 1.031384  | -0.906287 | -1.461649 |
| H         | 0.954795  | -0.687125 | 2.330209  |
| H         | 1.469827  | -1.741134 | 1.217457  |
| H         | 2.200171  | -0.300657 | 1.367293  |
| H         | -1.562368 | -0.075561 | -2.057387 |
| H         | -2.164499 | 1.026081  | -1.030941 |
| H         | -0.920427 | 1.407129  | -1.997678 |
| H         | 0.720576  | 2.417464  | -0.673103 |
| H         | 1.456396  | 2.012570  | 0.708929  |
| H         | 2.035037  | 1.469386  | -0.705342 |
| H         | -1.268573 | 1.945628  | 1.131574  |
| H         | -1.938671 | 0.562311  | 1.648358  |
| H         | -0.555137 | 1.092274  | 2.305603  |
| H         | -2.100953 | -1.540449 | -0.089489 |
| H         | -0.785633 | -2.487385 | -0.113283 |
| H         | -1.286385 | -1.839099 | 1.280812  |
| H         | 1.970246  | -1.220781 | -1.193406 |
| H         | 0.585346  | -1.741836 | -1.854485 |
| H         | 1.187132  | -0.301032 | -2.275043 |

## II. Force Field Parameters for Atomistic Simulations

**Table S2:** Simulation Force Field Parameters

| atom types          | potential type <sup>a</sup> | parameter    | value              |
|---------------------|-----------------------------|--------------|--------------------|
| Co-N                | harmonic bond <sup>b</sup>  | $k_b^c$      | 352.5              |
|                     |                             | $r_0$        | 1.94 Å             |
| Co-N                | rigid bond <sup>d</sup>     | $r^\ddagger$ | 2.05 Å             |
| N-H                 | rigid bond                  | $r$          | 1.03 Å             |
| Co-N-H              | harmonic angle              | $k_\theta^e$ | 30                 |
|                     |                             | $\theta_0$   | 114°               |
| H-N-H               | harmonic angle              | $k_\theta^e$ | 44                 |
|                     |                             | $\theta_0$   | 104°               |
| O-N                 | 12-6                        | $A^f$        | $8.78 \times 10^5$ |
|                     |                             | $B^g$        | $7.83 \times 10^2$ |
| H <sub>SPC</sub> -N | 12-6                        | $A^f$        | $6.09 \times 10^2$ |
|                     |                             | $B^g$        | 15.3               |
| N-N                 | 12-6                        | $A^f$        | $1.32 \times 10^6$ |
|                     |                             | $B^g$        | $1.03 \times 10^3$ |

<sup>a</sup> Functional forms of the potentials appropriate for the provided parameters are in accordance with the CHARMM<sup>5</sup> convention. <sup>b</sup> Parameter adapted from Ref. 6; <sup>c</sup> harmonic bond force constant reported in units of kcal/mol Å<sup>-2</sup>; <sup>d</sup> observed simulated transition state bond length in agreement with previously reported value;<sup>7,8</sup> <sup>e</sup> harmonic angle force constant reported in units of kcal/mol rad<sup>-2</sup>; <sup>f</sup> van der Waals 12-6 A parameter reported in units of kcal/mol Å<sup>12</sup>; <sup>g</sup> van der Waals 12-6 B parameter reported in units of kcal/mol Å<sup>6</sup>.

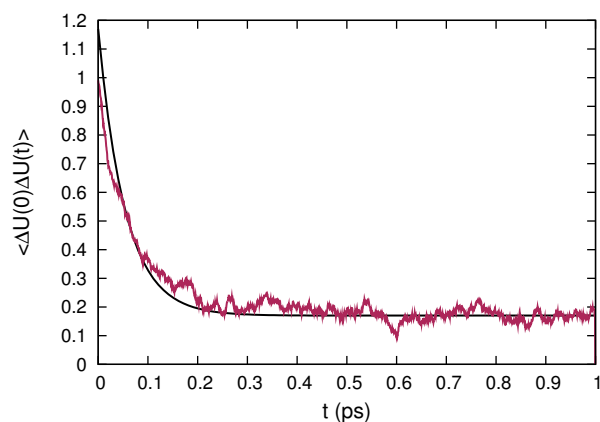
## III. Solvent Relaxation Timescales

We demonstrate the ability of the approach outlined in this work to provide insight into solvent relaxation timescales. Defining a collective coordinate  $\Delta U$  reminiscent of the solvent coordinate in Marcus theory,<sup>9</sup> the energy difference between the diabatic electronic states within the tight binding approximation is expressed as:

$$\Delta U(\mathbf{Q}) = -\frac{e}{4\pi\epsilon_0} \sum_{k=1}^N \left( \frac{q_k}{|\mathbf{Q}_D - \mathbf{Q}_k|} - \frac{q_k}{|\mathbf{Q}_A - \mathbf{Q}_k|} \right). \quad (1)$$

Here,  $q_k$  the charge on solvent atom  $k$ , and  $\mathbf{Q}_D$ ,  $\mathbf{Q}_A$ , and  $\mathbf{Q}_k$  positions of the “donor” Co center, “acceptor” Co center, and solvent atom  $k$ , respectively. Time resolving the auto-

correlation of  $\Delta U$  provides insight into the relaxation time of the solvent environment. In this study, an initial relaxation time of about 300 fs is indicated (Fig. S1), consistent with solvent relaxation on the same timescale of our electronic transition (shown by  $\kappa$  in Fig. 5 in the main text), followed by a second longer relaxation mechanism that extends beyond the simulation time.



**Figure S1:** The normalized autocorrelation function of  $\Delta U$  Eq. 1 along RPMD trajectory time.

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