Supporting Information for the Manuscript:

Photoinduced Electron Transfer in Donor-Acceptor Complexes: Isotope Effect and Dynamic Symmetry Breaking

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SI-1 Computational Details

Geometry optimizations were performed with the Amsterdam Density Functional program\textsuperscript{2,3} using Density Functional Theory (DFT). The BLYP exchange correlation functional\textsuperscript{4,5} was used in combination with a Slater type basis set of the triple zeta with one polarization function (TZP)\textsuperscript{6} quality. Dispersion corrections have been included following the formalism proposed by Grimme (DFT-D3)\textsuperscript{7}. The Ehrenfest dynamics simulations were performed with the Octopus program\textsuperscript{8–11}. A nucleus centered spherical grid with a maximum radius of 7.56 Bohr for real space discretization was used; tests have been performed to find the optimal spacing (0.375 Bohr), resulting in a 70.18 Rydberg cut off. Troullier-Martins pseudopotentials\textsuperscript{12} were used to describe the core electrons. The BLYP exchange-correlation functional\textsuperscript{4,5} has also been used for the Ehrenfest dynamics. The initial photoinduced electron configuration for the Ehrenfest dynamics was generated by moving one electron from the highest occupied β-orbital to the virtual β-LUMO+2. A time step of 1 attosecond was chosen to accurately describe the time evolution of the electrons. The initial nuclear velocities are set to zero; due to relaxation from the Franck-Condon point, the kinetic energy rises during the trajectory. We fix the nuclear coordinates of the nitrogen in the melamine tail as well as the oxygen in the isocyanuric tail (furthest from the hydrogen bond interface) to avoid translational motion of the complex and to maintain the relative distance, as would be the case due to the environment in a crystal or DNA backbone. This is also advisable since the electron transfer rate is distance dependent. In figure S1, we show the electron transfer time evolution for a trajectory with an intermolecular distance increased by 1 Å compared to the optimized geometry. As is clearly visible, this is already enough to inhibit the charge transfer process on the time scale of the simulation.
Figure S1. Comparison of electron transfer pattern starting from optimized geometry (black) and a geometry with an intermolecular distance increased by 1 Å (green). This increase in intermolecular distance is enough to inhibit the charge transfer process within the time scale investigated.

To quantify the electron transfer, we monitor the difference between electron densities with α- and β-spin ($\rho(\beta) - \rho(\alpha)$) during the trajectory. Excess of β-spin density therefore corresponds to the excited electron, deficiency of β-spin density represents the hole. This difference spin density was integrated over two halves of the simulation box, each containing the donor or acceptor molecule, respectively. The integrated density on the acceptor was then used to quantify the amount of electron density transferred during the Ehrenfest trajectory. A Fourier analysis of this electron transfer process was also done, using a gaussian window function with a sigma value of 0.8 to reduce noise. The initial geometries used for the Ehrenfest dynamics (non-symmetric and symmetric) are given in tables S1 and S2.
Table S1. Initial geometry (in Bohr) used for the Ehrenfest dynamics without enforced C$_{2v}$-symmetry with the fixed atoms marked with *

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| N    | -2.001614 | 0.031842 | 0.000000 |
| C    | -3.426373  | -2.135237 | 0.000000 |
| C    | -3.379525  | 2.278876  | 0.000000 |
| N    | -5.992697  | -2.227231 | 0.000000 |
| N    | -5.949866  | 2.399089  | 0.000000 |
| C    | -7.117530  | 0.115311  | 0.000000 |
| N    | -2.123401  | 4.418507  | 0.000000 |
| N    | -2.233755  | -4.326562 | 0.000000 |
| N    | -9.614457  | 0.117436  | 0.000000 * |
| H    | -0.114494  | 4.450706  | 0.000000 |
| H    | -3.121367  | 6.044066  | 0.000000 |
| H    | -3.274394  | -5.947841 | 0.000000 |
| H    | -0.239847  | -4.434270 | 0.000000 |
| H    | -10.533707 | 1.851824  | 0.000000 |
| H    | -10.585442 | -1.583609 | 0.000000 |
| C    | 8.517469   | -0.165043 | 0.000000 |
| N    | 7.061556   | -2.324476 | 0.000000 |
| N    | 7.095488   | 2.110390  | 0.000000 |
| C    | 4.427971   | -2.407892 | 0.000000 |
| C    | 4.517363   | 2.253758  | 0.000000 |
| N    | 3.358169   | -0.044253 | 0.000000 |
| O    | 10.757456  | -0.132269 | 0.000000 * |
| O    | 3.346296   | 4.294753  | 0.000000 |
| O    | 3.319715   | -4.429777 | 0.000000 |
| H    | 7.996239   | -3.989308 | 0.000000 |
| H    | 8.097476   | 3.783894  | 0.000000 |
| H    | 1.213266   | -0.002685 | 0.000000 |
Table S2. Initial geometry (in Bohr) used for the Ehrenfest dynamics with enforced C<sub>2v</sub>-symmetry with the fixed atoms marked with *

| Atom | X    | Y    | Z    |
|------|------|------|------|
| N    | -2.603536 | 0.000000 | 0.000000 |
| C    | -3.999683 | -2.168130 | 0.000000 |
| C    | -3.999683 | 2.168130 | 0.000000 |
| N    | -6.546495 | -2.279433 | 0.000000 |
| N    | -6.546495 | 2.279433 | 0.000000 |
| C    | -7.692047 | 0.000000 | 0.000000 |
| N    | -2.739492 | 4.396637 | 0.000000 |
| N    | -2.739492 | -4.396637 | 0.000000 |
| N    | -10.268718 | 0.000000 | 0.000000 | * |
| H    | -0.811858 | 4.473371 | 0.000000 |
| H    | -3.780779 | 5.997919 | 0.000000 |
| H    | -3.780779 | -5.997919 | 0.000000 |
| H    | -0.811858 | -4.473371 | 0.000000 |
| H    | -11.205478 | 1.663445 | 0.000000 |
| H    | -11.205478 | -1.663445 | 0.000000 |
| C    | 7.978317 | 0.000000 | 0.000000 |
| N    | 6.508749 | -2.192863 | 0.000000 |
| N    | 6.508749 | 2.192863 | 0.000000 |
| C    | 3.868282 | -2.314315 | 0.000000 |
| C    | 3.868282 | 2.314315 | 0.000000 |
| N    | 2.646694 | 0.000000 | 0.000000 | * |
| O    | 10.286523 | 0.000000 | 0.000000 |
| O    | 2.763579 | 4.365135 | 0.000000 |
| O    | 2.763579 | -4.365135 | 0.000000 |
| H    | 7.449109 | -3.869490 | 0.000000 |
| H    | 7.449109 | 3.869490 | 0.000000 |
| H    | 0.588848 | 0.000000 | 0.000000 |
SI-2 Excitation energies with Time dependent DFT

To classify important electronic excitations of the pseudo base pair system, linear-response time dependent DFT calculations were performed with ADF\textsuperscript{2,3}. Since BLYP\textsuperscript{4,5} is known to poorly describe charge transfer excitations, we calculated the first 30 excitations using also the long range corrected CAM-B3LYP\textsuperscript{13} exchange correlation functional and a TZp\textsuperscript{6} basis set with D3 dispersion corrections\textsuperscript{7}. The relative orbital alignment of the relevant orbitals for BLYP and CAM-B3LYP are given as energy differences in table S3.

Table S3. Orbital energy differences between HOMO/LUMO, LUMO/LUMO+1 and LUMO+1/LUMO+2 for BLYP and CAM-B3LYP.

| Energy Difference | BLYP (Hartree) | CAM-B3LYP (Hartree) |
|-------------------|---------------|---------------------|
| \(\Delta E_{\text{LUMO-HOMO}}\) | 0.129         | 0.308               |
| \(\Delta E_{\text{(LUMO+1)-LUMO}}\) | 0.009         | 0.006               |
| \(\Delta E_{\text{(LUMO+2)-(LUMO+1)}}\) | 0.038         | 0.031               |

As expected for a hybrid functional, the HOMO-LUMO gap is significantly increased in CAM-B3LYP in comparison to the GGA BLYP. However, there is no rearrangement in the four relevant orbitals active in the charge transfer process. Excitation energies and oscillator strengths for the most relevant excitonic and charge transfer excitations are reported in table S4. As expected for a GGA functional, BLYP strongly underestimates the charge transfer excitation energy. However, for both functionals, the energy of the excitonic state is higher in comparison to the charge transfer state. Furthermore, the oscillator strength of the excitonic state is in both cases larger than that of the charge transfer state.
**Table S4.** Excitation energies and Oscillator strength for the most relevant charge transfer and excitonic excitations in the melamine-isocyanuric acid pseudo base pair determined by TDDFT with BLYP and CAM-B3LYP.

|                        | BLYP          | CAM-B3LYP    |
|------------------------|---------------|--------------|
|                        | Energy [eV]   | Oscillator strength | Energy [eV]   | Oscillator strength |
| Charge transfer excitation | 3.680        | 0.0037       | 6.407        | 0.1220           |
| Excitonic excitation    | 6.1834        | 0.2767       | 6.905        | 0.6140           |
SI-3 Ehrenfest dynamics with frozen nuclear geometry

Electron dynamics simulations were performed with fixed nuclear degrees of freedom. Two different geometries were investigated: the initial geometry at the start of the Ehrenfest dynamics (from here on called simulation G0) and the geometry from the Ehrenfest trajectory at 10.7 fs, approximately the time where the electron transfer process starts (named simulation G1). The latter geometry lies therefore within the region where the involved electronic states are closely coupled. The total simulation time was 50 fs with a time step of 1 as. The integrated spin density on the acceptor as a function of time is shown in figure S2.

![Figure S2](image-url)  

*Figure S2.* Comparison of electron transfer pattern with free nuclear degrees of freedom (black) with fixed nuclear coordinates at the initial geometry (simulation G0, a, red) and with fixed nuclear coordinates at the geometry taken at 10.7 fs of the original trajectory, when the electron transfer starts (simulation G1, b, red).
In figure S3, a frequency analysis of the electron transfer patterns shown in figure S2 is presented. The peaks at around 4300 cm\(^{-1}\) and 5500 cm\(^{-1}\) corresponding to the trajectory with free nuclei show significant overlap with the frequencies of electron density oscillations in the case of the frozen initial geometry (simulation G0). This strongly suggests that the high frequency oscillations are due to the coupling between electronic states at a geometry close to the Franck-Condon point. The main peak at about 3500 cm\(^{-1}\) shows instead significant overlap with the electron density oscillation frequency extracted from simulation G1, where the nuclei were fixed at a geometry in the strong coupling regime. This is also the peak that has a large overlap with the N-H bond vibrations. This shows that at this specific geometry, a resonance between electronic energy difference and nuclear vibration (the N-H stretches) has emerged.

![Frequency analysis graph](image)

**Figure S3.** Frequencies of electron transfer processes: in black, ET pattern during Ehrenfest simulation with free nuclear degrees of freedom, in blue ET transfer frequencies at fixed nuclear degrees of freedom at initial geometry (simulation G0), in red ET transfer frequencies at fixed nuclear degrees of freedom with geometry at onset of electron transfer (approx. 10.7 fs, simulation G1).
SI.4 Assignment of relevant peaks in the total VDOS

The bond distances were extracted from the nuclear trajectory. Fourier Transforms (FT) were performed on these bond distances to obtain the corresponding vibrational frequencies. By performing a Fourier Transform on the velocity autocorrelation function, a total Vibrational Density Of States (VDOS) of the entire system was obtained. A gaussian window function with a sigma value of 0.8 was chosen to filter out noise in the Fourier transform consistently with the Fourier analysis of the electron transfer pattern. In order to assign specific peaks in the total VDOS, we analyze the time evolution of specific localized geometric parameters such as bond distances and angles extracted from the trajectory. Fourier transforms reveal the underlying frequencies. We find that the highest frequency band at $\approx 3500 \text{ cm}^{-1}$ can clearly be associated with N-H stretching modes as shown in figure S4. The N-H bond involved in the central N-H-N hydrogen bond shows instead a considerably lower frequency, giving rise to a red shifted peak in the total VDOS at $\approx 2700 \text{ cm}^{-1}$. This can be explained by the relatively strong hydrogen bond, with the hydrogen almost being shared between the two nitrogen atoms. As shown in figures S5 and S6, the peak centered around $1500 \text{ cm}^{-1}$ consists of several contributions from C=O stretches, C-N stretches and some bending modes. The overlap between many modes close in frequency make a direct association in the sub-$2000 \text{ cm}^{-1}$ range in general complicated. What clearly emerges through this vibrational analysis is the separation in frequency of the N-H bonds compared to all other vibrational modes.
Figure S4. VDOS of the pseudo base pair obtained via FT of the velocity autocorrelation function extracted from the Ehrenfest trajectory (black). Shown in color are all frequencies of the N-H stretches obtained via FT of the bond distances extracted from the Ehrenfest trajectory. The corresponding bonds are color-coded in the chemical structure above. Interesting is the shifted frequency of the central N-H bond on the donor-acceptor interface, as its frequency is significantly shifted to lower values due to the weakening of the bond through the strong hydrogen bond formed.
**Figure S5.** VDOS of the pseudo base pair obtained via FT of the velocity autocorrelation function extracted from the Ehrenfest trajectory (black). Shown in color are frequencies of C=O stretches and C-N stretches obtained via FT of the bond distances extracted from the Ehrenfest trajectory. The corresponding bonds are color-coded in the chemical structure above.
Figure S6. VDOS of the pseudo base pair obtained via FT of the velocity autocorrelation function extracted from the Ehrenfest trajectory (black). Shown in color are frequencies of ring vibrations obtained via FT of the bond distances extracted from the Ehrenfest trajectory. The corresponding bonds are color-coded in the chemical structure above.
Figure S7 shows the total VDOS for the two simulations using $^1$H and $^2$D respectively. The N-H (N-D) stretches are shifted as expected, the difference between frequencies of the central N-D bond being weakened by a strong hydrogen bond and all other N-D bonds decreases, thus both peaks merge. The former is still seen as a shoulder on the peak of the latter.

Figure S7. Total VDOS of the $^2$D substituted (red) and $^1$H systems (black), obtained by performing a Fourier Transform of the velocity autocorrelation functions using the respective trajectories.
SI.5 Dynamic Symmetry breaking

Figure S8. Time evolution of the orbital energies (a) of the LUMO+2 (red), LUMO+1 (dark blue) and LUMO (light blue) in comparison to the electron transfer (green, b) during the Ehrenfest dynamics simulation starting with a $C_2v$-enforced initial geometry.
Figure S9. Difference in bond distance between symmetry equivalent bond pairs. Here, the bond distance of the bonds shown as lower in the chemical structure is subtracted from the bond distance of their respective symmetry equivalent bond above. Color-coded are the four bond pairs first diverging from perfectly symmetric behavior.
SI.6 Dipole moment orientation

![Dipole moment orientation plot](image)

**Figure S10.** Orientation of the dipole moment associated with β-electrons in the x-y plane for the simulation with enforced symmetric starting geometry. The colors correspond to consecutive time intervals, starting from red (0-20 fs) over yellow (20-40 fs), green (40-60 fs), light blue (60-80 fs) and dark blue (80-100 fs). A rotational character is visible in this case as well, but seems to be obscured by the large change in x due to the generated charge transfer state.
**Figure S11.** Orientation of the dipole moment associated with $\alpha$-electrons in the x-y plane for the simulation without enforced symmetry. The colors correspond to consecutive time intervals, starting from red (0-20 fs) over yellow (20-40 fs), green (40-60 fs), light blue (60-80 fs) and dark blue (80-100 fs). Rotational character, yet noisy, is apparent also in this simulation.
SI-7 Estimated non-adiabaticity of the process via the two level model by Purchase et al.¹

Following the model discussed in Appendix A in Purchase et al ¹, we consider the formula for the period τ needed to convert the reactant state to the product state during the nonadiabatic process:

\[
\tau = \frac{\pi}{R_0 d_{12} \omega_n}
\]

We should keep in mind, that this result is obtained for a simple two state model that is coupled to a single nuclear vibrational mode of frequency \( \omega_n \) with displacement \( R_0 \). To get a rough estimate of the nonadiabatic coupling term \( d_{12} \) for our donor-acceptor molecular complex, we therefore choose the most relevant nuclear mode which is coupled to the electronic motion. We consider the case with symmetric starting conditions (figure 1c), where the central N-H bond vibration is the most relevant mode. Its frequency, \( \omega_n \) is determined to be roughly 2700 cm\(^{-1}\) (see figure S4). The displacement \( R_0 \) of this mode is determined from the trajectory to be approximately 0.04 Å (see figure 2a). As a rough estimate for the complete charge transfer process, we take the time from onset of electron transfer to end of the simulation (55 fs, see figure 1c) and multiply by 3 to extrapolate to full electron transfer. In this way we estimate a period \( \tau = 165 \) fs. By using these parameters extracted from our system, we estimate a value of 0.94 Å\(^{-1}\) for \( d_{12} \).
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