

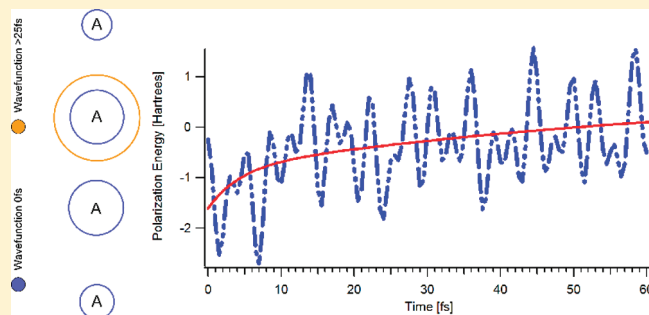
Localization of a Hole on an Adenine–Thymine Radical Cation in B-Form DNA in Water

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Supporting Information

ABSTRACT: A quantum mechanics/molecular mechanics (QM/MM) molecular dynamics (MD) simulation has been carried out using CP2K for a hole introduced into a B-form DNA molecule consisting of 10 adenine–thymine (A/T) pairs in water. At the beginning of the simulation, the hole wave function is extended over several adenines. Within 20–25 fs, the hole wave function contracts so that it is localized on a single A. At 300 K, it stays on this A for the length of the simulation, several hundred fs, with the wave function little changed. In a range of temperatures below 300 K, proton transfer from A to T is seen to take place within the A/T occupied by the hole; it is completed by ~40 fs after the contraction. We show that the contraction is due to polarization of the water by the hole. This polarization also plays a role in the proton transfer. Implications for transport are considered.



INTRODUCTION

There have been many studies, experimental and theoretical, of the properties of a hole on a DNA oligomer with a base sequence of A/T's and immersed in water. The hole, whatever its wave function, is properly called a polaron, this indicating that it is a compound particle in the sense that its wave function and motion are affected by the polarization of the surrounding water molecules. In an early study, among the first to emphasize the important effect of water on the properties of the hole, the hole wave function was assumed to be spread over a number of sites (adenines in this case). The Hamiltonian was taken to include a term for the interaction between the portions of the hole on the different sites (which includes the effect of the environment) in addition to the usual tight-binding term for nearest-neighbor hopping. The water was assumed to be a continuum. The result of this calculation was that in the steady state the hole is delocalized, its wave function extending over ~4 adenines.¹ In a set of other studies, with water also taken as a continuum, the Hamiltonian included the tight-binding term with modifications such that the solvation energy was included. The result of these studies was that in the steady state a hole on a sequence of guanines (G) is strongly localized on a single G.^{2,3} Calculations for a sequence of adenines suggested that a hole would be localized on a single A in a series of A's, but this result was not as certain.³

In a couple of the most recent considerations of this subject, simulations using the code CP2K^{4,5} were employed. CP2K is advantageous for calculations involving a hole on DNA because it incorporates a correction for the incomplete cancellation of the electron self-interaction, found to be a serious shortcoming of density functional theory (DFT) when applied to an odd electron system.^{6,7}

In QM/MM simulations with CP2K on a 10-mer of A/T's, it was found that, just after introduction of a hole, its wave function was delocalized over the bases in the QM region, consisting of 5A/T's and their associated sugars and backbone.^{4,5} After a few fs, the wave function began to contract, and by 20–25 fs, it was almost entirely on one adenine.⁵ We suggested some possible origins for the contraction of the polaron.⁵ One, following a suggestion of Mantz et al.,⁷ was that it is due to an electronegative nitrogen on adenine (N7 or N3) forming hydrogen bonds with water and in the process repelling the hole from all but one adenine. Another, suggested by the calculation of Kumar and Sevilla for proton transfer in G/C,⁸ was the contraction being due to a concentration of water molecules around the adenine. A third possibility is that the contraction is due to polarization of the water surrounding the hole.

In the present paper, we look further into the source of the polaron contraction, finding that it cannot be accounted for by the first two suggestions above. We conclude rather that it is due to the polarization of the surrounding water by the hole. We will discuss also the role of the polarization in the subsequent proton transfer. Implications for the transport properties of a hole on an A/T oligomer in water will be discussed.

SIMULATION

As noted above, CP2K was designed to overcome the incomplete cancellation of the electron self-interaction. In the calculations presented in this paper, as in ref 4, a Kohn–Sham

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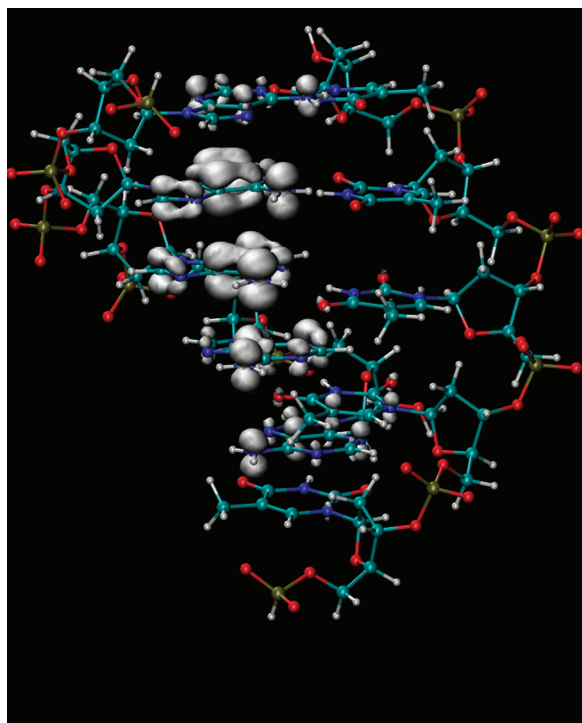


Figure 1. Initial wave function of the hole for a “300 K” run. $m(\mathbf{r}) = 0.001$.

energy functional expression at the restricted open shell DFT Becke–Lee–Yang–Parr, ROBLYP, level was employed, to which an empirical self-interaction correction^{6,7} was added. Another relatively unique feature of CP2K is that it employs a mixed Gaussian (a double ζ valence basis set with polarization functions (DZVP) in this case) and an auxiliary plane wave basis.

As described in ref 5, the QM/MM MD simulations were carried out with CP2K on a 10-mer, A/T duplex of canonical B-DNA that was generated using the AMBER 9 software suite.⁹ To prepare the system, 18 Na^+ counterions, matching the number of phosphates, were placed along the backbone, and the initial structure was equilibrated. Following this minimization, the system was solvated with a truncated octahedron of ~ 3000 TIP3P waters such that the edge of the waterbox is a minimum of 6 Å from any atom in the system. The system was again minimized, restraining the DNA atoms with a $500 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$ force constant and then minimized once more without restraints on any of the atoms. Five contiguous A/T base pairs (numbers 4 through 8) and their sugar plus backbone atoms were chosen as the quantum system, with one electron removed to introduce a hole. All minimizations were carried out before the hole was introduced.

Two simulations were carried out, one with an initial temperature of 20 K and the other with an initial temperature of 300 K, both with a time interval of 0.5 fs. The time length of the simulation was 600 fs for the former case and 230 fs for the latter. In both cases, the temperature was not kept constant but allowed to rise with time. A copy of the CP2K input file is in the Supporting Information. To plot the wave functions, we used the calculated spin density, $m(\mathbf{r})$.

RESULTS AND DISCUSSION

In both simulations, we found the initial wave function spread out over the five adenines in the QM region. Very little of the wave function was found on the thymines. In Figure 1, we show

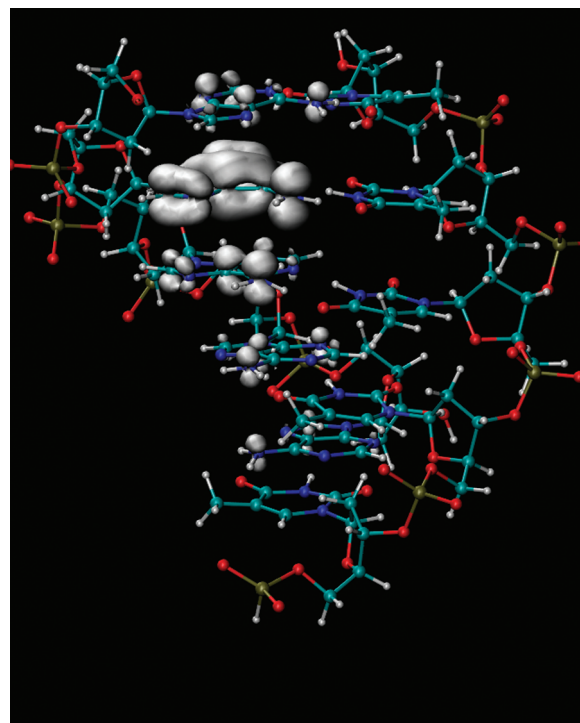


Figure 2. Wave function of the hole after 18 fs for a “300 K” run. $m(\mathbf{r}) = 0.001$.

the initial wave function for one particular “300 K” run (the runs were characterized by the initial temperature). Up to the time the contraction is complete, the behavior of the wave function is quite similar for the two different temperature runs. In what follows, unless we are talking about proton transfer, we will mainly direct our attention to the “300 K” run where proton transfer was not found. Another example of the initial wave function is shown in Figure 2 of ref 4. It is seen in this example and in Figure 1 of this paper that the wave function peaks at one A and decreases, not necessarily monotonically, on successive A's. We note that, although the polaron seen in Figure 1 and in ref 4 looks quite similar to the polaron calculated with continuum water,¹ their origin is not the same. The polaron of ref 1 represents a steady state arising from the balance of the tendency for the hole to move freely along the DNA chain (quantum delocalization) with the confining force due to the polarization of the water by the hole (solvent localization). The polaron of Figure 1, however, does not represent a steady state. Just after the introduction of the hole, the polaron does not see a polarized medium. Its wave function is limited in extent, rather than infinite, because the polaron is confined to the defined QM region—a short section of the chain.

As time progresses, the wave function amplitude starts changing after ~ 10 fs; it decreases on all but one adenine. In Figure 2, taken at 18 fs, the amplitude on the fifth A is seen to have grown at the expense of the others. This process continues rapidly until, by ~ 20 fs, the wave function is almost entirely on adenine 5. Defining the volume of the hole as the volume containing 95% of its spin, we find that the decrease of the hole volume with time is described by Figure 3 for the “300 K” run. Also in Figure 3, we show the evolution of the temperature for the “300 K” run with time.

Searching for the reason for the polaron contraction, we investigated the distribution of water molecules in the “300 K” run.

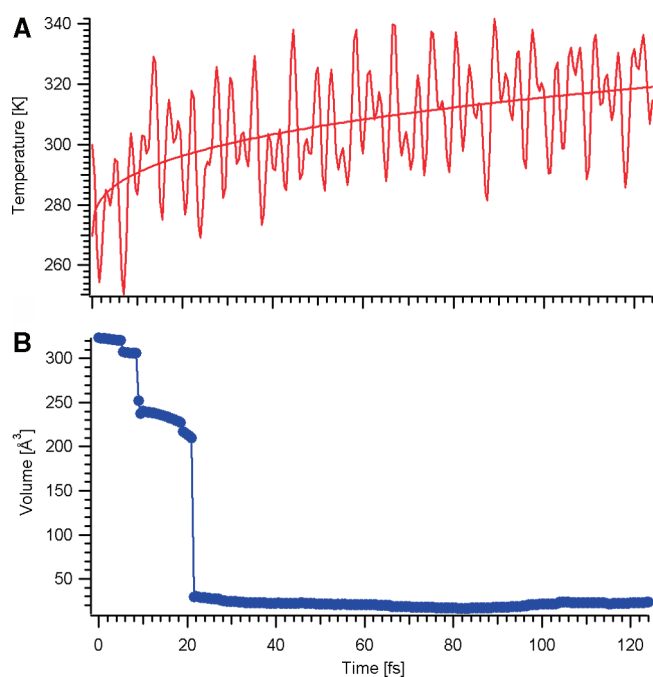


Figure 3. (A) Temperature as a function of time for a “300 K” run.²⁵ (B) Volume of space enclosed by the hole for a “300 K” run.

Specifically, we looked for water molecules in five spheres of radius 8 Å, centered on N1, N3, N6, N7, and N9 of the adenine on which the hole is located, and then in such spheres on all the other adenines. We found that, around the adenine with the hole, during the time the polaron contraction was taking place the closest water molecules were still at least 4 Å away, precluding the formation of hydrogen bonds. For the other adenines, there were one or two oxygens between 3 and 4 Å from N3 or N7, but their orientation was such that the hydrogens bonded to them could not form a bond with N3 or N7. With time, diffusion brings water molecules closer, but the earliest any appropriately oriented water molecule is seen to come within bonding distance is ~ 150 fs, well beyond the time scale in which the polaron contraction occurs. These findings rule out the possibility of the contraction mechanism being the elimination of the hole wave function from all but one adenine by formation of hydrogen bonds between the electronegative nitrogens and water hydrogens on all the other adenines. The simulations of Mantz et al. gave evidence for such bonds being formed in picoseconds,⁴ presumably when diffusion brings the water molecules close enough.

The finding of such a low concentration of water near the adenines also rules out the possibility of a mechanism involving a high concentration of water molecules around the A with the hole. It should be noted that the calculation of Kumar and Sevilla, showing that a high water concentration around the G/C is favorable for proton transfer in G/C, was carried out for an isolated G/C in solution.⁸ Such concentrations are unfavorable in a B-DNA structure because of the hydrophobic nature of the bases. In fact, the water molecules we found in the neighborhood of the adenine with the hole were almost entirely in the major groove.

As regards the third possibility for explaining the contraction, we show first that the polarization of the water by the hole can rise from close to zero to a significant amount in the ~ 20 fs during which the contraction takes place. It is well-known that the response of a solvent to a change in solute charge distribution

is strongly bimodal. For water, it is generally accepted that there is an initial ultrafast response due mainly to librational motion of the solvent molecules, followed by a slow component due to diffusive motion.¹⁰ In water, there are two librational modes, L1 (wavelength 25 μm) and L2 (15 μm), with resonant frequencies of ~ 11.5 and 23 THz.¹¹ The former, more abundant mode, has a period of ~ 88 fs, the latter ~ 50 fs. According to their frequencies, these modes are at least partially excited at 300 K. The periods are small enough to allow rotations of the water dipoles and thus account for a rising polarization in the 5–20 fs time range.

Contraction of the polaron due to polarization of the surrounding water satisfies the data in other respects also. Although, according to Figure 3, after a short initial drop the temperature is rising during the entire “300 K” run, the calculated potential energy of the system, shown in Figure 4, is decreasing over most of the range. Note that the energy of the system is almost entirely potential energy, less than 1% being kinetic energy. The rate of decrease is most rapid during the first 20 fs, where the big changes in the hole wave function are taking place, and less rapid thereafter, the average energy coming to a plateau after ~ 150 fs. It is difficult to quantify the energy fall because initially there are fluctuations of more than 2 hartree (a Hartree is 27 eV) on a fs scale, but the change in the average potential energy over the first 20 fs appears to be a sizable fraction of a Hartree. Of course, the energy will be a function of the amount of water included in the calculation. There is similar behavior in the “20 K” run, although the initial energy fall and temperature rise are steeper, the major part of both taking place during the first 10 fs.

Another feature of the data, seen in Figure 3, is that there are two time periods in which the rate of decrease of the polaron volume is small, specifically 0–5 fs and 10–20 fs. We speculate that in the 0–5 fs interval the lower frequency libration L1 is building up to the point where the water polarization it gives rise to can have a relatively strong effect on the volume of the polaron. At that point, ~ 5 fs, the volume of the polaron decreases abruptly by $\sim 25\%$. It then takes some time for water molecules to fill in the regions opened up by the contraction and for the L2 vibration, with the higher frequency, to build up. We suggest that 20 fs represents the time for these processes to increase the polarization, now due to the two modes, sufficiently to complete the polaron contraction. For the “20 K” run, the decrease of the polaron volume with time is also small in the 0–5 fs interval, after which the volume decreases abruptly by about 20%, similar to the case at “300 K”. Again, the contraction is relatively small for the next interval, ~ 20 fs in this case, in which time the water molecules are filling in the regions opened up by the contraction and the L2 mode, as well as the L1 mode, is presumably increasing in amplitude. The final, big contraction takes place at ~ 25 fs, a little later than for the “300 K” run. The fact that the final contraction takes place a few fs later for the “20 K” run could be due to the lower average temperature, ~ 125 K in this time range for the “20 K” run.

Having established that the time scale for growth of the water polarization is compatible with the time scale for contraction of the polaron, and that the variation of the energy and hole volume with time can, qualitatively at least, also be accounted for by the water polarization, we show now that energy considerations are consistent with the contraction being the result of water polarization. We have seen that the water polarization has the effect of decreasing the polaron energy. In the case where the hole wave function is spread out over a number of A's, the polarization is spread over the water surrounding these A's, having a peak around each A.

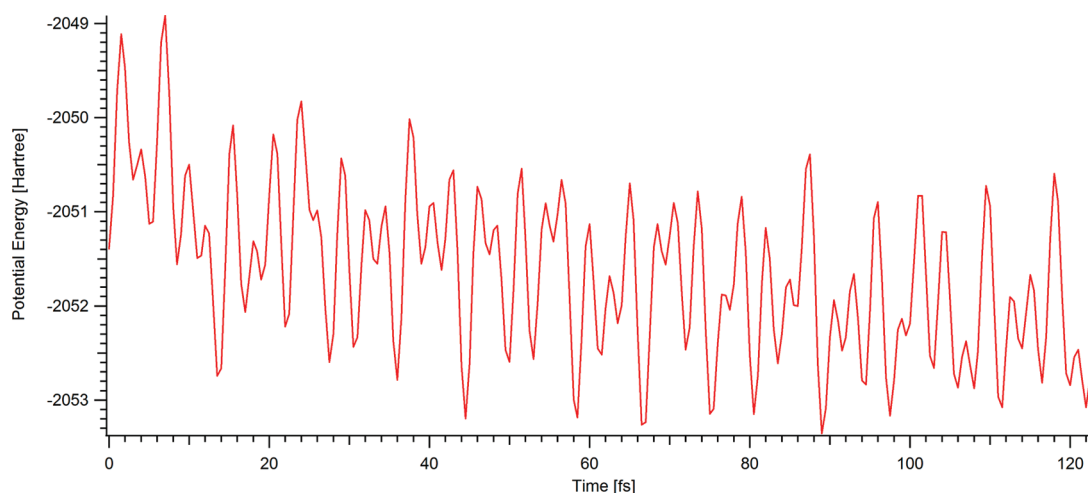


Figure 4. Potential energy of the system as a function of time for a “300 K” run.

The total lowering of energy due to the polarization is a sum of the lowering experienced at each adenine. When the wave function is contracted to a single A, all of the polarization is centered at that site. The water dipoles are all then as close to that site as possible, and in reorienting make their maximum contribution to the energy lowering. Thus, the contracted polaron has lower energy than any arrangement in which the polaron is spread out over a number of bases.

We consider now the role played by the water polarization in proton transfer. It is seen in Figure 2 of ref 5 that the shift of the proton to the thymine begins at ~ 15 fs, even before the contraction is complete. It is clear that the shift decreases the repulsion of the hole and the proton for each other. The resulting energy decrease is undoubtedly enhanced by a shift in the total polarization in response to the change in position of the proton. Thus, the stability of the proton transferred state in the A/T duplex arises from a very different mechanism than that found by Kumar and Sevilla for an isolated G/C in solution.⁸ We suggest that the details of the mechanism for proton transfer in a G/C duplex¹² are similar to those we found for the A/T duplex in the time subsequent to the contraction.⁵

For G/C duplexes, it was predicted by Steenken^{13,14} and later observed by Adhikary et al.¹² that the proton-transferred state would be the dominant species at ambient temperature because it is the thermodynamically stable state. For A/T in the temperature range 120–220 K, our simulation gave the proton-transferred state. Above 260 K, our simulation gave A/T in the state A^{*+}/T . Of course, in equilibrium, both states must exist over the temperature range.

The results of the simulations and further consideration of the source of the contraction that we have carried out lead to the conclusion that the stable state for a hole on an A/T duplex in water is a polaron localized on one adenine. As discussed earlier, this was not the conclusion arrived at in some earlier treatments, theoretical and experimental, which we will now reexamine.

In the picture of Basko and Conwell,¹ as noted earlier, the extent of the polaron is determined by two factors: the tendency of the polaron to spread, determined by t_0 , the transfer integral (or the bandwidth $4t_0$), and the tendency of the polarization of the surrounding water to make it contract. Using the value for t_0 of a pair of adjacent adenines assumed to be reasonable at the time of their calculation, 0.2 eV, they arrived at the conclusion that the steady-state polaron would spread over four adenines.

Since then, more careful calculations for a pair of neighboring adenines have obtained a t_0 value of 0.03 eV.^{15–17} According to the formulation of Basko and Conwell, this value of t_0 would reduce the steady-state size of the polaron to one site. More recent calculations of the coupling of adjacent A's, taking into account the enhancement due to thermal vibrations, have obtained a value of 0.06 eV,¹⁸ which would allow the size of the polaron to be ~ 1 to 2 sites. In any case, there is not a serious discrepancy between the polaron size obtained with the discrete water calculation and the continuum calculation.

With the stable state for the hole being a polaron localized on a single site, transport on an all A/T duplex should be mainly by polaron hopping between A's. Note that this differs from the polaron hopping picture of Schuster et al. in that the polarons on that picture were expected to be ~ 4 bases in length and to be characterized by uneven spacing of the bases within the polaron.¹⁹ According to the results of our calculations and those of ref 4, such polarons are not found in an all A/T duplex DNA.

Barton has suggested that there is an additional contribution to charge transfer from delocalized polarons, domains formed transiently due to the motions of the bases and water molecules creating charge-transfer active conformations.²⁰ An experiment that has been cited as evidence for a delocalized hole domain spread over three or four A's, is that of O'Neill and Barton.²⁰ In the experiment, optical excitation of 2-aminopurine (Ap) creates a hole next to Ap in the sequence $Ap(A)_nG$. In the picture that a hole occupies a single site, as n increases from unity, the number of holes that reach G would be expected to decrease monotonically. Instead, O'Neill and Barton found the number reaching G decreased as n increased from 1 to 3 but then reached a peak at $n = 4$ before decreasing again and then reaching a second, lower peak at $n = 8$. This was interpreted as evidence for a delocalized domain, transiently formed, occupying four A's.²⁰ On the evidence of the calculations presented above, however, there is a big difference in energy between the situation where the hole is spread over four A's and when it is localized on a single A, the former being a sizable fraction of a Hartree larger than the latter. This indicates that, if a delocalized domain is formed in the O'Neill–Barton experiments, it cannot consist of a series of A/T's but must include also the terminal G/C. Therefore, there is no reason to believe that the mechanism suggested by Barton and O'Neill can contribute to transport in an all A/T duplex.

One other mechanism that could contribute to charge transport is superexchange, which could be considered a type of tunneling. Superexchange is coherent orbital-mediated tunneling where (for holes) the high energy LUMOs on the pathway between the initial and final sites (A's in our case) are virtually occupied. Because it is basically tunneling, the probability of this process occurring falls off rapidly with the distance between the initial and final sites. Some groups claim to have seen evidence for superexchange through one, two, or three A's, while other groups find that this process does not occur at all. It can only be concluded that it is not clear whether superexchange results in significant transport through a series of A/T's.

It has been widely considered that the more rapid transport observed for a hole on a series of A's than on a series of G's is due to the hole being delocalized over a number of A's while it is localized on G. A reason why transport could be more rapid in a series of A's than in a series of G's, even though the wave function is limited to one site in each case, is related to the different nuclear reorganization energy (NRE) involved in formation of the cation radical in the two cases. The formation of $G^{\bullet+}$ in the G/C base pair requires an NRE of 0.34 eV,^{21–23} whereas formation of $A^{\bullet+}$ in A/T requires only 0.10 eV.^{21–23} In the latter case, the cation radical has nearly the same structure as the neutral, making it easier for the hole to hop.

Our finding that a hole in a series of adenines on a duplex in water is localized to a single A, plus the finding of Voityuk^{2,3} that a hole on a series of G's is localized to a single G, may not mean, however, that even in the steady state a hole is limited to a single base whatever the base sequence. For a set of experiments measuring charge transport in duplexes with periodic base sequences such as (AGGA)_n or (ATTA)_n, it was found that the data could be fit by a simple kinetic analysis which assumed that a single hop took the hole from the *n*th sequence to the *n*+1th.²⁴ This suggested that the hole wave function is spread over an AGGA or ATTA sequence.

■ ASSOCIATED CONTENT

S Supporting Information. CP2K input file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) It may be noted that Figure 3 is the same as Figure 3A in ref 5 except that the time unit there is stated as fs rather than 0.5 fs. The labeling on this Figure 3 is the correct one. No error resulted in ref 5 because the only error was in the labeling of the figure.