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Charge migration in polycyclic norbornadiene cations: Winning the race against decoherence

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The observation of electronic motion remains a key target in the development of the field of attoscience. However, systems in which long-lived oscillatory charge migration may be observed must be selected carefully, particularly because it has been shown that nuclear spatial delocalization leads to a loss of coherent electron density oscillations. Here we demonstrate electron dynamics in norbornadiene and extended systems where the hole density migrates between two identical chromophores. By studying the effect of nuclear motion and delocalization in these example systems, we present the physical properties that must be considered in candidate molecules in which to observe electron dynamics. Furthermore, we also show a key contribution to nuclear delocalization arises from motion in the branching plane of the cation. For the systems studied, the dephasing time increases with system size while the energy gap between states, and therefore the frequency of the density oscillation, decreases with size (obeying a simple exponential dependence on the inter-chromophore distance). We present a system that balances these two effects and shows several complete oscillations in the spin density before dephasing occurs. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4965436]

I. INTRODUCTION

Recent years have seen the development of sub fs pulses and the emergence of the field of attoscience.[1,2] Attosecond spectroscopy promises the prospect of real time observation of electronic motion, such as charge migration,[3] on its native time scale.[2,4–7] In charge migration, several cationic states are populated coherently upon ionization of a neutral species, forming a non-stationary state where the hole oscillates between sites in the molecule (this is in contrast to charge transfer that is driven by nuclear motion). A central theoretical challenge is to suggest molecular systems where such electron dynamics might be observed experimentally.

In previous work,[8–11] we have shown that we can engineer electron dynamics near a conical intersection. However, we have also demonstrated that nuclear spatial delocalization, due to the zero-point energy of the neutral species, can "wash out" the electron density oscillations[12–14] because of the spread of the energy gaps in the nuclear wavepacket. In this article, we study norbornadiene (NBD) and poly-cyclic-norbornadiene (PLN) systems (see Figure 1), where the charge migration occurs between two ethylenic cation moieties. The rigid "scaffold" controls the distance between the ethylenes. Because the energy gap has a simple exponential distance dependence, we can control the energy gap by extending the scaffold. In this way, several oscillations in the electron density can take place before decoherence occurs. Further, we show that the decoherence arises mainly from nuclear delocalization in the branching space,[15] of the cationic conical intersection. This suggests that by making the scaffold more rigid in the branching space one might significantly delay decoherence.

The phenomena of charge migration in molecules have been extensively studied theoretically. Considering a single static nuclear geometry, the solution of the time-dependent electronic Schrödinger equation (in a.u.) for a two-state wavepacket reads

$$\Psi(\mathbf{r},t;\mathbf{R}) = c_0 e^{-iE_0(\mathbf{R})t}\psi_0(\mathbf{r};\mathbf{R}) + c_1 e^{-iE_1(\mathbf{R})t}\psi_1(\mathbf{r};\mathbf{R}), \quad (1)$$

where $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear coordinates, respectively. The hole oscillates with a frequency defined by the energy gap of the states involved,

$$T(\mathbf{R}) = \frac{2\pi}{\Delta E}. \quad (2)$$

Starting from this, theoretical studies predict long-lived hole migration at a well-defined frequency,[3,16–23] by not considering the induced nuclear motion or the nuclear spatial delocalization (as a result of the zero-point energy).

Previous theoretical studies have shown the system dependence of the effect of nuclear motion using the Ehrenfest method.[8,10,11] Our studies on para-xylene[12] and phenylamines[13] showed that the electron dynamics was not destroyed by the nuclear motion over the studied timeframe (~20 fs) but the frequency and amplitude was altered, in agreement with studies on methyl substituted benzenes.[11]

Only recently has the nuclear delocalization been taken into account in theoretical studies,[12–14] where it has been demonstrated that it, in general, will lead to a loss in electron density oscillations, with the time scale being system dependent. In the neutral ground vibrational state, the nuclear

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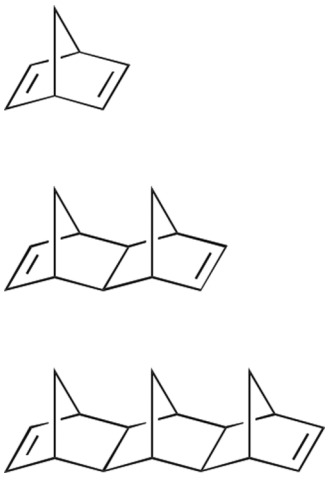

FIG. 1. Structures of the three molecules studied. *Top:* norbornadiene (NBD), *middle:* 2-ringed PLN (PLN2), *bottom:* 3-ringed PLN (PLN3). Geometries optimized with B3LYP/6-31G* are given in S1.

positions are delocalized. This delocalization leads to a spread of energy gaps between the cationic states, and therefore a spread in the period of the electron dynamics (Eq. (2)). The cumulative effect over time is that the spread in frequency of the electron dynamics causes the oscillations to dephase, resulting in a loss of the overall density oscillation. The time scale of this dephasing depends on the width of the energy gap distribution, i.e., how spread the oscillation frequencies are. The energy gap distribution is affected by the width of the ground state nuclear wavepacket and by the gradients of the cationic states involved. In the same systems (para-xylene and phenyl-amines), we showed the nuclear spatial delocalization due to the zero point energy quickly led to loss of the overall density oscillation; this occurred on a longer time scale in the 3-ringed poly-cyclic norbornadiene.

In this article, we shall study norbornadiene and its poly-cyclic analogues, where we extend the scaffold size by increasing the number of rings from 1 to 3, and for simplicity name these systems PLN2 and PLN3 (see Figure 1). It has been shown both experimentally[24–26] and theoretically[27,28] that the two lowest cationic states of norbornadiene correspond to ejection of an electron from the symmetric and antisymmetric combination of the ethylenic π bond orbitals and that these states are well separated from higher states (>2 eV). In the present work, we assume ionization with an appropriate broad bandwidth pulse creates an equal superposition of these two lowest cationic states; such a coherent superposition has been created with many states in phenylalanine.[7] Alternatively, a spatially localized excitation would lead to the ionization of one π orbital, forming a coherent population of the two delocalized cationic states. Upon creation of this non-stationary electronic wavepacket, the hole becomes localized and oscillates between the two π systems of the double bonds with a frequency defined by the energy gap (Eq. (2)). Because the distance between the ethylenic moieties increases, the energy gap must decrease; therefore, the period of oscillation increases. Further, as the number of rings increases the skeletal vibrations become more delocalized and "softer." Thus the dephasing happens at a later time.

II. COMPUTATIONAL METHODS

In our simulations, the cationic electronic states are found via the complete active space self-consistent field (CASSCF) method using a 6-31G* basis, where the two π and two π^* orbitals are included in a CAS(3,4) active space. Equation (1) is then propagated in time. The movement of the unpaired electron is observed by following the spin density (the difference between α and β density). We choose to directly observe the changes in spin density as it is a more sensitive indicator than the overall electron density; however, the same conclusions could be drawn from the total density or the dipole moment (see Section S4 in the supplementary material).

As stated, fixed nuclei studies alone are not sufficient to identify candidate systems in which to observe electron dynamics, so we must go beyond this standard approach and study how nuclear motion affects the electron dynamics. As in previous studies, we simulate the effect of nuclear motion using our CASSCF based Ehrenfest implementation,[10,29,30] where the electronic degrees of freedom are treated quantum mechanically and the nuclei propagated classically (here a time step of approx. 0.1 fs is used). This method fully accounts for non-adiabatic couplings.[10]

To study the 2nd nuclear effect, that of nuclear spatial delocalization, we generate a set of geometries (using NewtonX[31]) to represent the ground state vibrational wavepacket by sampling a Wigner distribution[32] around the neutral minimum. This is a quantum distribution in classical phase space. Care is taken to ensure that convergence of the sampling is reached; this requires 1000 geometries for the 1-ring system and 500 for the 2- and 3-ring systems. Electron dynamics (fixed nuclei) simulations are carried out separately at each geometry of the distribution. In recent work, we showed that allowing the nuclei to move has little effect on the dephasing time.[14]

III. RESULTS AND DISCUSSION

In Figure 2 we show the oscillation in spin density for the 3 systems, starting from the optimized geometry of the neutral, for fixed nuclei simulations (solid lines). The relevant time constants and potential energy constants are given in Table I. In all systems, the spin density oscillates between the two ethylenic moieties. Note that the energy gap correlates well with the period of oscillation according to Eq. (2) and shows a simple dependence on the distance R. As the scaffold size increases, the energy gap decreases, showing approximately an exponential decay of the energy gap with distance due to the decay of the overlap integral (see Figure 3 and Section S2 in the supplementary material for explanation). Therefore the period of oscillation increases as the number of rings increases.

The effect of nuclear motion is not large in these systems (dashed lines in Figures 2(a) and 2(b)) only affecting the

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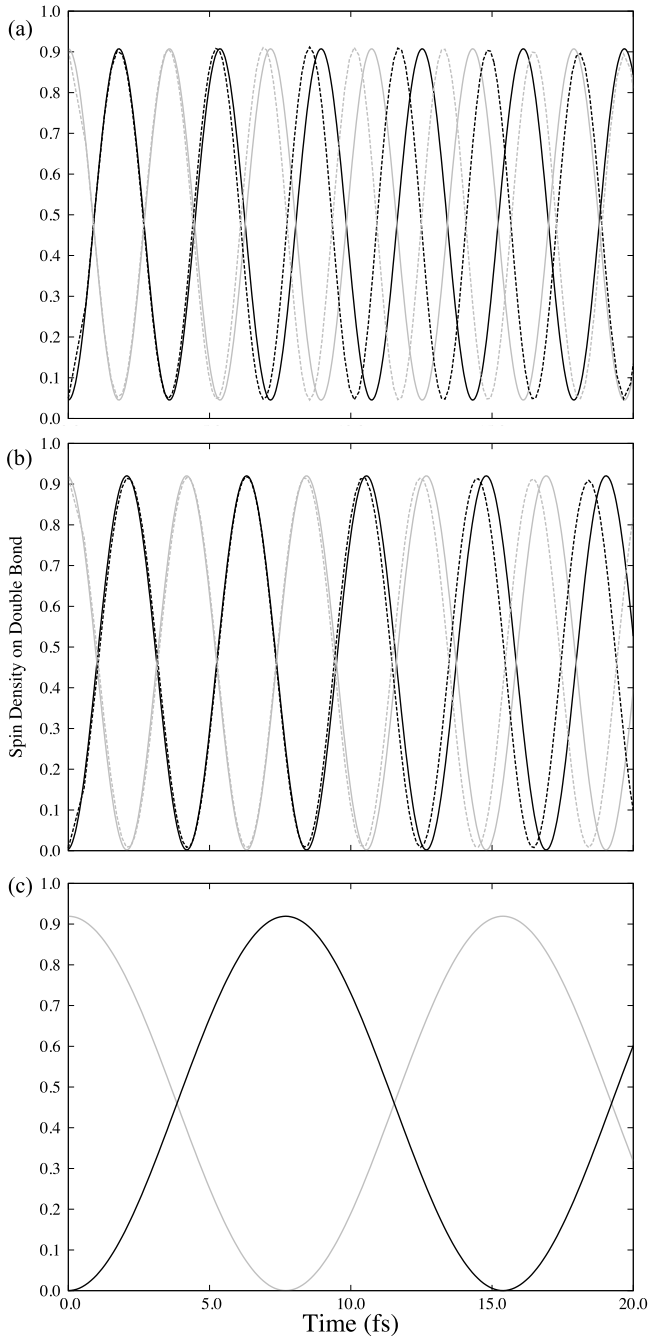

FIG. 2. Spin density on the double bonds following ionization of (a) NBD, (b) PLN2, (c) PLN3. Black lines indicate spin density on one double bond, gray on the other. Solid/dashed lines indicate the result of fixed/moving nuclei simulations (no simulation with moving nuclei for PLN3, panel (c)).

frequency of the oscillation (energy gap increases). As with the previously reported results, nuclear motion does not have a significant effect and does not destroy the electron dynamics in these systems, on this time scale.

To study the effect of nuclear delocalization, we simulate the electron dynamics at each geometry of the distribution, before taking the average to be our overall spin density value. In the bottom half of Table I, we give corresponding characteristics of the sample of geometries. In Figure 4, we show the spin density on one of the double bonds through time for the geometries that sample the Wigner distribution

TABLE I. Energy gaps (ΔE) and magnitude of the gradient differences (Δg) between cationic states in the three systems at the neutral equilibrium geometries (R is the distance between ethylenic moieties), and the resulting period of oscillation (T), calculated using CASSCF(3,4)/6-31G*. Also given are the average energy gap of the Wigner distribution ($\overline{\Delta E}$) and the standard deviation (σ). The average period ($\bar{T}$) is found via Eq. (2). $t_{\frac{1}{2}}$ is the estimated half-life of the average oscillation for the ensemble of geometries and $n_{\frac{1}{2}}$ is an indicator of the number of complete density oscillations before the amplitude is halved.

	1-Ring	2-Ring	3-Ring
At minimum			
R (Å)	2.49	4.72	7.06
ΔE (eV)	1.15	0.98	0.27
T (fs)	3.58	4.24	15.30
Δg	0.08	0.05	0.02[a]
Of ensemble			
$\overline{\Delta E}$ (eV)	1.14	1.00	0.36
$\sigma(\Delta E)$ (eV)	0.23	0.13	0.12
$\bar{T}$ (fs)	3.63	4.14	11.50
$t_{\frac{1}{2}}$ (fs)	2.90	6.40	10.00
$n_{\frac{1}{2}}$	0.80	1.55	0.87

[a]Calculated using STO-3G, for justification see the supplementary material.

around the minimum geometry of the neutral species, with the average spin density indicated in white. The average period of oscillation increases with scaffold size (number of rings) and is similar to the central geometry (T and $\bar{T}$ in Table I). This also correlates well with the average energy gap and the inter-chromophore distance R. In all systems, dephasing occurs such that the overall average spin density loses its oscillatory behavior and tends to a constant value where the average spin density is delocalized between the two π systems (see Section S5 in the supplementary material). In general the dephasing rate decreases with system size. Why? The dephasing is controlled by the width of the energy gap distribution, which is in turn controlled by the gradient difference. The magnitude of this gradient difference ($\Delta g = |\frac{\partial(E_1 - E_2)}{\partial \mathbf{R}}|$, given in Table I) increases as the number

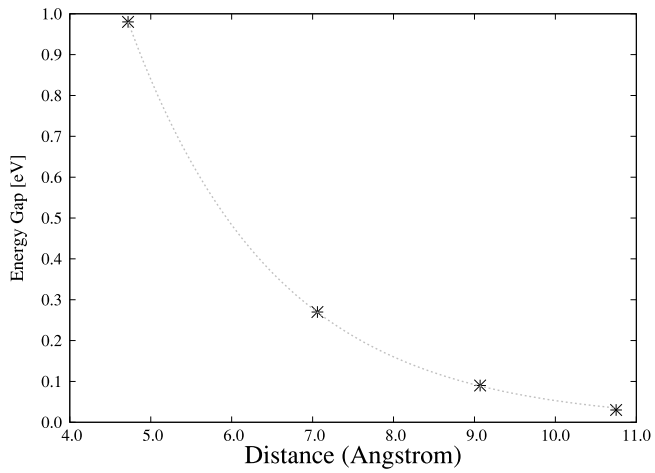

FIG. 3. The relation of the energy gap between cationic states and the distance between the π bonds when increasing scaffold size from PLN2 to PLN5. The dashed line indicates the fitted exponential $\Delta E(R) = 13.29e^{-0.55R}$.

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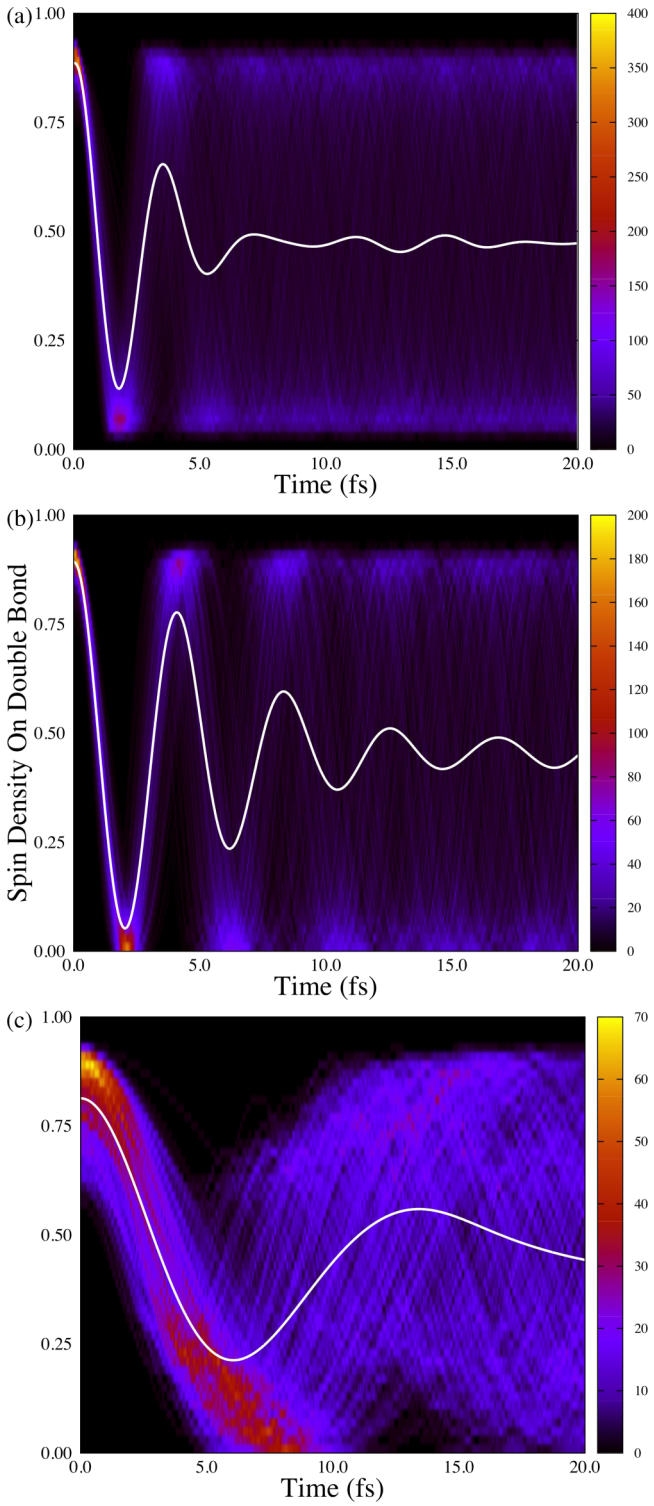

FIG. 4. Electron dynamics for the ensemble of nuclear geometries around (a) NBD, (b) PLN2, (c) PLN3. The white line represents the average spin density value.

of rings decreases, leading to a wider energy gap distribution, resulting in quicker dephasing. This dephasing is due to the continuous distribution of oscillation frequencies within the width of the nuclear wavepacket; therefore, once dephasing occurs revivals are not expected.

We can compute the number of complete oscillations of the average spin density before the amplitude is halved $n_{\frac{1}{2}} = t_{\frac{1}{2}}/\bar{T}$; this is shown in Table I. Note that we have the optimum situation in PLN2 where the energy gap is small enough to allow 1.5 oscillations ($n_{\frac{1}{2}}$) before dephasing ($t_{\frac{1}{2}}$) occurs. In contrast for NBD the width is large and the period is small, and in PLN3 the period is large and the width is small, resulting in both cases in $n_{\frac{1}{2}} < 1$.

Because the difference between the gradients of the cationic states, previously indicated in the model to be of key importance, is one of the branching space vectors, one can assume that the distortions in the branching space of the conical intersection of the cation will have the greatest effect on the energy gap distribution (the branching space vectors are indicated in Figure 5). The importance of the branching space distortions can be illustrated more starkly. For the 1-ring case, we artificially removed the cationic branching space distortions from the geometries of the Wigner distribution around the neutral molecule. Figure 6 shows that this increases the half-life of the spin density oscillation by a factor of 2. This shows that a longer half-life can be obtained in the 1-ring system via chemical modification to

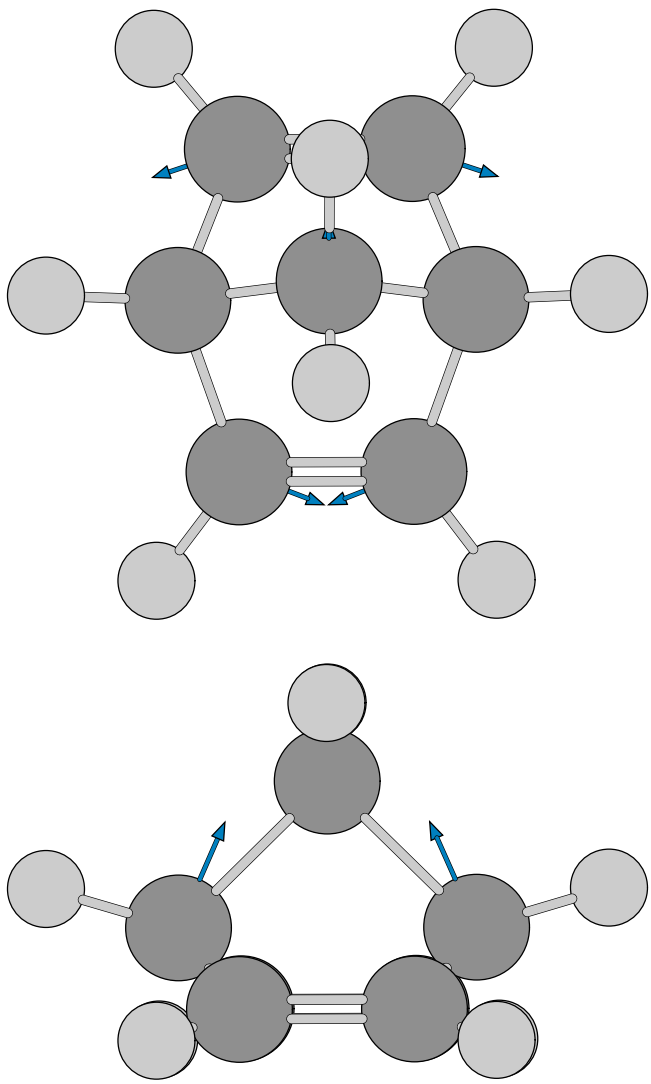

FIG. 5. Branching space vectors at the conical intersection of NBD. *Top:* gradient difference vector, magnitude: 0.1068. *Bottom:* derivative coupling vector, magnitude: 0.0863.

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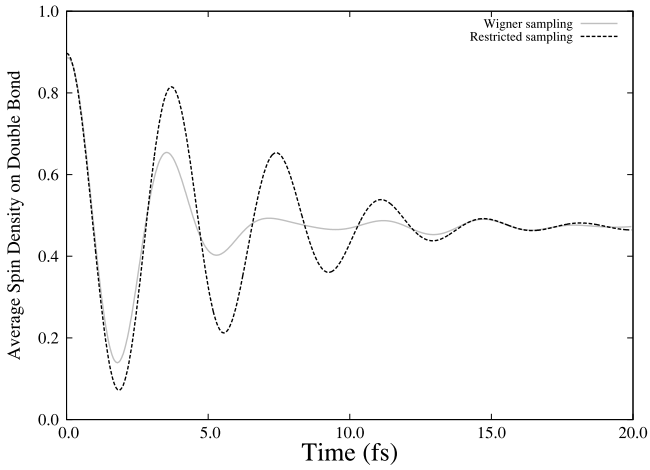

FIG. 6. Average spin density on one double bond for the Wigner distribution of nuclear geometries around NBD ("Wigner") (as in Fig. 4(a)) and for the ensemble when the branching space distortions are removed ("restricted").

restrict motion in the branching space vectors. This restriction in these degrees of freedom occurs naturally in the 2 and 3 ring cases, hence their longer half-life. When selecting candidate systems for observing electron dynamics, the degree of spatial delocalization of the neutral molecule in the cationic branching space must be a general consideration because of the effect on the distribution of energy gaps between states.

IV. CONCLUSIONS

In summary, through the example of polycyclic norbornadienes, we have shown the general properties that must be considered when looking for candidate systems in which to observe electron dynamics.

We have demonstrated electron dynamics between π systems in norbornadiene systems. The energy gap between states is dependent on the distance between the π systems; therefore, by extending the framework the period of the electron density oscillation can be increased. Allowing nuclear motion, within the Ehrenfest approximation, does not destroy the electron dynamics in the 1- and 2-ring systems up to the studied time of 20 fs.

The zero-point energy of the neutral molecule leads to dephasing of the electron density oscillations in all systems, with varied time scales. We rationalize the dephasing times in terms of wavepacket width and the gradient difference of the states involved. Engineering of the energy gap gives a system (PLN2) that shows several complete oscillations in the spin density before dephasing.

We have also demonstrated that vibrations of the neutral molecule in the branching space of the cation have a large effect on the dephasing time. Restriction of vibrations in these vectors can extend the half-life. Such restrictions could be achieved via chemical substitution, as suggested here.

SUPPLEMENTARY MATERIAL

See the supplementary material for structural information, explanation of the energy gap trend, gradient difference comparisons, and more.

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