Next Generation QTAIM for the Design of Emitters Exhibiting Thermally-Activated Delayed Fluorescence (TADF) with Laser Irradiation

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The effect of a static electric (**E**)-field and an unchirped and chirped laser pulse field on the cycl[3.3.3]azine molecule was investigated using next-generation quantum theory of atoms in molecules (NG-QTAIM). Despite the magnitude of the **E**-field of the laser pulses being an order of magnitude lower than for the static **E**-field, the variation of the energy gap between the lowest lying singlet (S₁) and triplet (T₁) excited states was orders of magnitude greater for the laser pulse than for the static **E**-field. Insights into the response of the electronic structure were captured by NG-QTAIM, where differences in the inverted singlet-triplet gap due to the laser pulses were significant larger compared to those induced by the static **E**-field. The response of the S₁ and T₁ excited states, as determined by NG-QTAIM, switched discontinuously between weak and strong chemical character for the static **E**-field. In contrast, the response to the laser pulses to induce polarization effects in the form of 'mixed' bond types. Our analysis demonstrates that NG-QTAIM is a useful tool for understanding the response to laser irradiation of the lowest-lying singlet S₁ and triplet T₁ excited states of emitters exhibiting thermally-activated delayed fluorescence (TADF). The chirped laser pulse led to more frequent instances of the desired outcome of an inverted singlet-triplet gap than the unchirped pulse, indicating its usefulness as a tool to design more efficient OLED devices.

1. Introduction

Recent work demonstrated that lasers can create strong light-matter interactions that are known to exert selective effects on electronic states of different spin multiplicity[1]–[3]. Control of the low-lying excited states is required to be able to optimize the photo-physical properties of the candidate organic emitter or absorber molecule for a given application. More recently, an alternative pathway to the harvesting of triplet excitons has been proposed. This is based on the phenomenon of thermally activated delayed fluorescence (TADF), which is believed to be one of the most promising routes to increase the efficiency of organic light-emitting diode (OLED) devices [4]. In the TADF process, a small gap between the lowest-lying singlet and triplet state $\Delta E(S_1$ - T_1) enables a thermal up-conversion from the triplet to the singlet manifold and as a consequence fluorescence from the not very bright S₁ state. The design principle for emitters exhibiting TADF is the minimization of the singlet-triplet gap to enable fast reverse intersystem crossing (ISC), or even an inverted singlet-triplet gap $\Delta E(S_1-T_1)$, where $\Delta E(S_1-T_1) < 0[4]$. There is a growing interest, however, in designing molecules with an inverted singlet-triplet gap $\Delta E(S_1-T_1)$, which would allow replacing the up-conversion in TADF with a more efficient down-conversion[5]–[11]. The systematic design of inverted singlet-triplet gap $\Delta E(S_1-T_1)$ emitters is currently challenging because the S₁ state is not very bright, rendering the discovery of such molecules difficult. For example, cycl[3.3.3]azine violates Kasha's rule[12] and displays a stronger emission from the S₂ state. A recent four-state model [13] proposed by de Silva et al. explained the possibility of efficient TADF as a consequence of mixing of diabatic charge-transfer (CT) and local excitation (LE) states, which resulted in mixed-character adiabatic states that enabled simultaneously small $\Delta E(S_1-T_1)$ with relatively high spin-orbit coupling and oscillator strength. Recent review articles highlight the computational and theoretical developments in the field [14]–[17]. Sampling of the resultant parameter space of the model yielded solutions with negative singlet-triplet gaps, which indicate such outcomes are feasible for real molecular systems. Various other mechanisms have been identified as feasible routes to overcome the exchange interactions and lead to negative singlet-triplet gaps. These include constrained density functional theory calculations undertaken by Difley et al., which indicate inversion is possible in exciplexes. This was explained in terms of the kinetic exchange mechanism stabilizing singlet states[18]. The presence of a polarizable environment was found by Olivier *et al.* to also lead to stabilization of singlets, which enables negative $\Delta E(S_1-T_1)$ [19]. The effect of a microcavity on a molecule was discovered by Eizner et al. to give rise to inverted polaritonic states [20]. Another route to creating inverted states is inhibition of internal conversion in the triplet manifold, so that T₂ is the lowest populated triplet state and is located above S_1 [21].

All investigations to date, however, do not provide the ability to provide a qualified *ab initio* prediction of an OLED with $\Delta E(S_1-T_1) < 0$ [22]. This due to the lack of understanding of the requirements from the electronic structure of a molecule needed to exhibit a negative energy gap. Experimental[23]–[26] investigations have demonstrated that for many TADF molecules the lowest triplet state is a local excitation (LE), suggesting that

that the understanding of the TADF mechanism needs to be reconsidered along with design strategies.

The goal of this investigation is to provide new tools to understand the directional response of the chemical bonding to two methods to perturb cycl[3.3.3]azine, which is a negative energy gap OLED. Firstly, we will consider a static electric(E)-field of ± 0.20 a.u. Secondly, we will use chirped and unchirped laser pulses of 100 fs duration with an experimentally accessible E-field = ± 0.02 a.u. to determine the effect on the S₁ \rightarrow T₁ energy difference and compare with the previously described static E-field. The time scale of the laser pulse is faster compared to that T₁ \rightarrow S₁ or S₁ \rightarrow T₁ transitions since the latter is thermally activated, therefore the ability to account for the response of electrons is highly relevant.

We will use recent developments of next generation QTAIM (NG-QTAIM), a directional, vector-based approach suited to capture the inherently directional and symmetry breaking phenomena associated with OLEDs in response to external agents such as **E**-fields and laser irradiation. The current conventional computational treatments are inadequate because they reduce the response of a given molecule to external agents to a set of scalar-based measures either using conventional QTAIM, orbital or orbital-free electronic structure methods. Earlier developments of NG-QTAIM were previously used for scoring molecular wires in **E**-fields for molecular electronic devices[27]. This will allow us to assess the topological stabilization/destabilization effects that perturbations of the static **E**-field and chirped/unchirped laser pulses have on the NG-QTAIM properties corresponding to the S₁ and T₁ states.

2. Theory and Methods

2.1 QTAIM BCP and bond-path properties

QTAIM is used to obtain critical points in the total electronic charge density distribution $\rho(\mathbf{r})$ by analyzing the gradient vector field $\nabla \rho(\mathbf{r})[28]$. These critical points are ordered according to the set of ordered eigenvalues $\lambda_1 < \lambda_2 < \lambda_3$, with corresponding eigenvectors $\mathbf{e_1}$, $\mathbf{e_2}$, $\mathbf{e_3}$ of the Hessian matrix of the total charge density $\rho(\mathbf{r})$. The complete set of critical points along with the bond-paths of a molecule or cluster is referred to as the molecular graph[29]. The most and least preferred directions of electron accumulation are $\mathbf{e_2}$ and $\mathbf{e_1}$, respectively [30]–[32]; the eigenvector $\mathbf{e_3}$ indicates the direction of the bond-path at the bond critical point (*BCP*). The ellipticity $\varepsilon = |\lambda_1|/|\lambda_2| - 1$, where λ_1 and λ_2 are negative eigenvalues of the corresponding eigenvectors $\mathbf{e_1}$ and $\mathbf{e_2}$, respectively. The ellipticity ε quantifies the relative accumulation of $\rho(\mathbf{r_b})$ in the two directions perpendicular to the bond-path at a *BCP*. The bond-path length (BPL) is defined as the length of the path traced out by the $\mathbf{e_3}$ eigenvector of the Hessian of the total charge density $\rho(\mathbf{r})$, passing through the *BCP*, along which $\rho(\mathbf{r})$ is locally maximal with respect to any neighboring paths [33]. The deviation from linearity of a bond-path separating two bonded nuclei is defined as the dimensionless ratio (BPL - GBL)/GBL of the difference between the BPL and the geometric bond length (GBL) and the GBL.

The NG-QTAIM interpretation of the chemical bond as the *bond-path framework set* \mathbb{B} , where $\mathbb{B} = \{p,q,r\}$ and

for a given electronic state a bond is comprised of three 'linkages'; p, q and r associated with the \underline{e}_1 , \underline{e}_2 and \underline{e}_3 eigenvectors, respectively. The p and q are 3-D paths constructed from the values of the least (\underline{e}_1) and most (\underline{e}_2) preferred directions of electronic charge density accumulation along the bond-path, referred to as r. For further discussions on the construction of bond-path framework set $\mathbb{B}[27]$, [34]–[43], see the **Supplementary**

Materials S2.

Using *n* points r_i along the bond path *r* (associated with eigenvector \underline{e}_3) and defining ε_i as the ellipticity at this point, one can draw vectors q_i and p_i , scaled by ε_i , originating at this point. The tips of these vectors (q_i and p_i) define the paths *p* and *q*. The form of p_i and q_i is defined as follows:

$$\boldsymbol{p}_{i} = \boldsymbol{r}_{i} + \varepsilon_{i} \underline{\boldsymbol{e}}_{1,i}, \, \boldsymbol{q}_{i} = \boldsymbol{r}_{i} + \varepsilon_{i} \underline{\boldsymbol{e}}_{2,i} \tag{1}$$

We will now define the extent to which the $\{p,p'\}$ path-packet constructed from the \underline{e}_1 eigenvector wraps i.e. *precesses* about a bond-path, see the left panel of **Scheme 1**. For the $\{p,p'\}$ path-packet, defined by the \underline{e}_1 eigenvector, we wish to follow the extent to which the $\{p,p'\}$ path-packet precesses about the bond-path by defining the *precession* \mathbb{K} for bond-path-rigidity [44]–[46]:

$$\mathbb{K} = 1 - \cos^2 \alpha$$
, where $\cos \alpha = \underline{\mathbf{e}_1} \cdot \underline{\mathbf{u}}$ and $0 \le \mathbb{K} \le 1$ (2)

Where $\underline{\mathbf{u}}$ defines the *BCP* \rightarrow *RCP* (bond critical point to ring critical point) path. Considering the extremes of \mathbb{K} , with α defined by equation (2), for $\mathbb{K} = 0$, there is maximum alignment of the *BCP* \rightarrow *RCP* path with the $\underline{\mathbf{e}_1}$ eigenvector, the least facile direction. For $\mathbb{K} = 1$ we have the maximum degree of alignment with the $\underline{\mathbf{e}_2}$ eigenvector, the most facile direction. In other words, $\mathbb{K} = 0$ and $\mathbb{K} = 1$ indicate bond-paths with the lowest and highest tendencies towards bond-path-flexibility, respectively. The precession \mathbb{K} is determined relative to the *BCP*, in either direction along the bond-path towards the nuclei at either end of the bond-path using an arbitrarily small spacing of $\underline{\mathbf{e}_1}$ eigenvectors. If we choose the precession \mathbb{K} of the {*p*,*p'*} path-packet about the bond-path when the $\pm \underline{\mathbf{e}_1}$ eigenvector is parallel to $\underline{\mathbf{u}}$, the *BCP* will have minimum facile character, i.e. bond-path-rigidity. By following the variation of the precession \mathbb{K} we can quantify the degree of facile character of a *BCP* along an entire bond-path.



Scheme 1. The construction of the $\{p,p'\}$ precession \mathbb{K} corresponding to the S₀, S₁ and T₁ states of the cyclazine molecular graph. The unit vector $\underline{\mathbf{u}}$ (blue arrows) is defined by the *BCP* \rightarrow *RCP* separation. The pale magenta line indicates the interatomic surface paths (IAS) that originate at the *BCP*. The undecorated green and red spheres indicate the locations of the *BCPs* and *RCPs* respectively

The precession \mathbb{K} provides the directional interpretation of chemical bonding necessary for laser induced symmetry breaking phenomena of electronic charge density distributions. The presence of values of the precession \mathbb{K} in the range $0 \le \mathbb{K} \le 1$ indicates polarization of the electron density $\rho(\mathbf{r})$ associated with the bondpath in terms of the changing orientation of the $\underline{\mathbf{e}}_1$ eigenvectors, from parallel to perpendicular, including intermediate orientations of the $\underline{\mathbf{e}}_1$ eigenvector. Consequently, there will be a range of 'mixed' bond types within the limits of the rigid shared-shell character $\mathbb{K} = 0$, characteristic of sigma bonds, and flexible closed-shell character $\mathbb{K} = 1$, characteristic of hydrogen bonding.

In this investigation, therefore, the molecular graph of cycl[3.3.3]azine is perfectly planar and therefore we will consider that polarization effects are indicated by the presence of any values of the precession \mathbb{K} between the upper and lower limits of $\mathbb{K} = 0$ and $\mathbb{K} = 1$ respectively.

3. Computational Details

The geometry optimized cycl[3.3.3]azine structures without the applied laser were obtained at the CISD/ccpVDZ theory level using the QChem code [47] along with the corresponding singlet S_0 , S_1 and triplet T_1 states. The static electric (E)-field results were obtained at the CASSCF (6,6)/cc-pVDZ theory level using the OpenMOLCAS code [48]. The laser pulse parameters used were: phase = 0, E-field strength = 0.02 a.u. aligned parallel to the C7-N9 bond-path, laser central frequency matching energy = 0.35 eV, sinusoidal pulse shape 0.0 to 100.0 fs, with 1.0 fs rise and fall times. For the quadratic chirped pulse (inset of Figure 1(b)), the parameter in the frequency domain $b_2 = 1000 \text{ fs}^{-2}$ [49]. For the quantum mechanics: the ground-state structure was optimized using OpenMOLCAS at the CAS(RASSCF) (6,6)/6-31G* level, state averaged over the three lowest CI roots, with spin-orbit coupling. For the dynamics, the same configuration was used for the singlet S_0 , S_1 and triplet T₁ states. At least ten instances of initial conditions were sampled from a Wigner distribution for each set of laser conditions and run as dynamics trajectories, with one instance from each set afterwards selected as representative. Properties were sampled every 0.5 fs, with 25 intermediate dynamics steps. The SHARC hopping algorithm [49] was used with spin-orbit coupling contributions included, states in diagonal representation, spin-corrected and fully adiabatic. An energy decoherence parameter of 0.1 a.u. was used [50], with frustrated hops not reflected and all electronic states active. At selected points along the dynamics trajectories, the natural orbitals of the singlet (S_1) and triplet (T_1) states were analyzed using the AIMALL software suite [51]. Subsequently, the resulting molecular graphs were analyzed using two in-house codes linked to the visualization toolkit Mayavi [52], to plot the p- and q-paths that comprise the QTAIM bond-path framework sets and the precessions \mathbb{K} .

4. Results and Discussion

The relative energy (inverted) gap $\Delta E(S_1-T_1) = -0.157$ eV for the case of static electric-(E)-field applied parallel to the C7-N9 *BCP* bond-path, see **Figure 1(a)** and **Scheme 1**. When subject to a constant E-field = -0.20 a.u. the inverted energy gap is widened, $\Delta E(S_1-T_1) = -0.159$ eV, and conversely narrowed for an E-field = +0.20 a.u., $\Delta E(S_1-T_1) = -0.155$ eV, see **Figure 1(a)**.

The relative energy gaps $\Delta E(S_1-T_1)$ for the lowest lying singlet (S_1) and triplet (T_1) excited states for the unchirped and chirped laser pulses, parallel to the C7-N9 bond-path, are presented in **Figure 2(a)** and **Figure 2(b)**, respectively. Note that the laser **E**-field strength = 0.02 a.u. which is an order of magnitude smaller than that of the static **E**-field.

A selection of the precessions \mathbb{K} are presented in Figures 2-4; the remaining \mathbb{K} are provided in the Supplementary Materials S3. We provide for comparison, as an inset figure in the left panel of sub-figure (a), the \mathbb{K} corresponding to the S₁ and T₁ states for the no laser or static E-field cases, in Figures 3-4. In addition, an inset figure of the labelled *BCP* is provided in the right panel of sub-figure (a) in Figures 3-4. Due to the stochastic nature of the dynamics trajectories, we will present the precessions \mathbb{K} without attempting to undertake further detailed quantitative analysis, such as integrations to determine areas under the \mathbb{K} plots. We will, however, present the precessions \mathbb{K} in a manner that allows comparison of the \mathbb{K} plots corresponding to the static E-field and the presence of laser irradiation.



Figure 1. The cycl[3.3.3]azine lowest-lying singlet (S₁) and triplet (T₁) states with the applied (+0.2/-0.2) **E**-field that is oriented parallel/anti-parallel to the C7-N9 *BCP* bond-path is presented in sub-figure (**a**), see **Scheme 1**. The values of the precessions K along the C10-N9 *BCP*, C10-C2 *BCP* and C10-C14 *BCP* bond-paths corresponding to the S₁ and T₁ excited states for an applied electric(**E**)-field = ± 0.2 a.u are presented along with the corresponding precessions K for an **E**-field = 0 in sub-figures (**b**-d).

Examination of the precessions \mathbb{K} without the static **E**-field indicates that the values of \mathbb{K} are only $\mathbb{K} = 0.0 \text{ or } \mathbb{K} = 1.0$. The presence of maximal bond-path flexibility for most of the extent of these bond-paths is indicated by $\mathbb{K} = 1.0$, see **Figure 1(b-d)**. The profile of the precessions \mathbb{K} possesses discontinuous jumps between $\mathbb{K} = 0.0$ and $\mathbb{K} = 1.0$ for the C10-N9 *BCP*, C10-C2 *BCP* and C10-C14 *BCP*. For the C10-N9 *BCP*, the region of maximal bond-path rigidity ($\mathbb{K} = 0.0$) occurs in the vicinity of the N9 atom. Conversely, a region of minimal bond-path rigidity ($\mathbb{K} = 1.0$) occurs close to the C atoms for the C10-C2 *BCP* and C10-C14 *BCP*. For the C10-C2 *BCP* and C10-C14 *BCP*. For the C10-C14 *BCP* bond-paths the T₁ state possesses a larger extent along the bond-path, towards the C10 atom in each case, with maximal bond-path rigidity ($\mathbb{K} = 0.0$) than is the case for the S₁ state. The application of the static **E**-field on the selected bond-paths has a negligible effect on either of the S₁ and T₁ states, where the \mathbb{K} values are only $\mathbb{K} = 0.0$ or $\mathbb{K} = 1.0$.

The relative energy gaps $\Delta E(S_1-T_1)$ of the lowest-lying singlet (S_1) and triplet (T_1) of the applied unchirped and chirped laser field can be seen by examination of **Figure 2**.



Figure 2. The cycl[3.3.3]azine lowest-lying singlet (S₁) and triplet (T₁) where the (+/-) **E**-field orientation is parallel/antiparallel to the C7-N9 *BCP* bond-path, see **Scheme 1**. The $\Delta E(S_1-T_1)$ values of cycl[3.3.3]azine subject to unchirped laser pulses (left panel) and chirped laser pulses (right panel). The **E**-field was aligned parallel to the C7-N9 bond-path. Note, values of $\Delta E(S_1-T_1) < 0$ are contained within the blue shaded region and red shaded region. Black dotted lines indicate for the chirped pulse 10 fs, 45 fs, 67 fs, 90 fs ($\Delta E(S_1-T_1) > 0$) and red dashed lines for the chirped pulse 5 fs, 30 fs, 78 fs, 100 fs ($\Delta E(S_1-T_1) < 0$) in the left panel. For the unchirped pulse (right panel) the blue dashed lines indicate 30 fs, 40 fs, 50 fs, 75 fs ($\Delta E(S_1-T_1) > 0$) and black dotted lines indicate 5 fs, 10 fs, 60 fs, 65 fs ($\Delta E(S_1-T_1) < 0$).

The profiles of the K corresponding to the positive energy gap $\Delta E(S_1-T_1) > 0$ with the unchirped laser pulse are generally characteristically different from the other profiles, in that the S_1 and T_1 profiles are separated from each other, see the left plot of **Figure 3(a)-Figure 4(a)**. This separation of the K profiles indicates that the T_1 states are more stable than the S_1 states on the basis of the greater tendency towards K = 0.0 for the T_1 states. The profiles of the K for the C10-N9 *BCP* with the unchirped laser pulse corresponding to the S_1 state at a given time with $\Delta E(S_1-T_1) > 0$ display a smaller response than the corresponding T_1 state at the same time, see the left panel of **Figure 3(a)**. The corresponding K for the C10-N9 *BCP* with $\Delta E(S_1-T_1) < 0$ and unchirped pulse result in a mixing of the K profiles of the S_1 and T_1 states, see the right panel of **Figure 3(a)**. The effect of the chirped laser pulse on the K profiles with a positive energy gap $\Delta E(S_1-T_1) > 0$ is to mix up the K profiles of the S_1 and T_1 states, see the left panels of Figure 3(b)-Figure 4(b). Conversely, the effect of the chirped pulse on the K profiles with a negative energy gap $\Delta E(S_1-T_1) < 0$ is to contract, or increase the sharpness of, the transition between the K = 0.0 and K = 1.0 profiles to closer resemble the K profile without the laser irradiation, see the right panels of Figure 3(b)-Figure 4(b) and the inset profile of left panel Figure 3(a)-Figure4(b).



Figure 3. The values of the precession \mathbb{K} along the C10-N9 *BCP* bond-paths for the S₁ and T₁ states. The unchirped pulses with a positive energy gap $\Delta E(S_1-T_1) > 0$ are presented in the left panel of sub-figure (**a**) at 30 fs, 40 fs, 50 fs and 75 fs and with a negative energy gap $\Delta E(S_1-T_1) < 0$ at 5 fs, 10 fs, 60 fs and 65 fs (right panel of sub-figure (**a**)). The chirped pulses with $\Delta E(S_1-T_1) > 0$ are presented in the left panel sub-figure (**b**) at 10 fs, 45 fs, 67 fs and 90 fs and with $\Delta E(S_1-T_1) < 0$ (right panel of sub-figure (**b**)) at 5 fs, 30 fs, 78 fs and 100 fs. The left inset figure of sub-figure (**a**) displays the corresponding S₁ and T₁ states without the laser present. The highlighted C10-N9 *BCP* on the molecular graph is indicated by the orange circle on the right inset of sub-figure (**b**), see the caption of **Figure 1** and **Scheme 1** for further details.



Figure 4. The values of the precession \mathbb{K} along the C10-C14 *BCP* bond-paths for the S₁ and T₁ states of the unchirped pulses 30 fs, 40 fs, 50 fs and 75fs with $\Delta E(S_1-T_1) > 0$ (left panel of sub-figure (a)), the unchirped pulse 5 fs, 10 fs, 60 fs and 65 fs with $\Delta E(S_1-T_1) < 0$ (right panel of sub-figure (a)). The values of the precession \mathbb{K} of the chirped pulses of chirped pulse 10 fs, 45 fs, 67 fs and 90 fs with $\Delta E(S_1-T_1) > 0$ (left panel of sub-figure (b)) and the chirped pulses at 5 fs, 30 fs, 78 fs and 100 fs with $\Delta E(S_1-T_1) < 0$ (right panel of sub-figure (b)). See the caption of **Figure 3** for further details.

The symmetry breaking effect of both the chirped and unchirped laser pulses are apparent from the continuous distribution of the precession \mathbb{K} values, see **Figure 3** and **Figure 4**. This symmetry breaking occurs because the nuclear positions shift slightly as a consequence of the application of the laser fields, but on much longer timescales than the response of the electronic charge density distribution. The nuclear positions also shift slightly as a consequence of the applied static **E**-field, but no symmetry breaking effects, in the form of continuous \mathbb{K} values, are apparent because the corresponding electronic charge density distribution is allowed to relax to an energetic minimum, see **Figure 1**.

5. Conclusions

We have provided new measures, in the form of the precession \mathbb{K} , to determine the response of the lowest-lying singlet (S₁) and triplet (T₁) states of cycl[3.3.3]azine to a static electric-(**E**)-field as well as an unchirped and chirped laser pulse. The precession \mathbb{K} yielded new insights into the behavior related to the electronic structure of a negative energy gap $\Delta E(S_1-T_1) < 0$, which is particularly useful due to S₁ being a not very bright state and therefore difficult to detect.

The application of a static **E**-field = -0.20 a.u. widened the negative energy gap $\Delta E(S_1-T_1) < 0$ by only 0.002 eV and reversing the **E**-field direction (= 0.2 a.u.) narrowed the negative energy gap by only 0.002 eV. Differences in the response of the precession K to the static **E**-field and the absence of an **E**-field were negligible. Therefore, the directional interpretation of the chemical bonding of the cycl[3.3.3]azine is that the directional characteristics of the bonding remains almost unchanged in response to the applied static electric-(**E**)-field, either taking values of K = 1.0 (weak, closed-shell *BCP* character) or K = 0.0 (strong, shared-shell *BCP* character).

The use of unchirped and chirped laser pulses with an E-field with a magnitude of only 0.02 a.u. and 100 fs duration however, created regions of negative energy gaps $\Delta E(S_1-T_1) < 0$ and positive energy gaps $\Delta E(S_1-T_1) > 0$ that were orders of magnitude greater than was the case for the application of the static E-field.

The response of the \mathbb{K} to the laser pulses was very significant, where in all cases the effect was to remove the discontinuous transitions along the bond-paths between these two bonding character extremes. This indicates the unique ability of the laser pulses to induce polarization effects in the form of the smooth continuous twisting of the $\{p,p'\}$ path-packet, as determined by \mathbb{K} possessing values *between* $\mathbb{K} = 1.0$ and $\mathbb{K} = 0.0$. This has the consequence of mixed bonding character types, between the extremes of the rigid shared-shell character bonds, for $\mathbb{K} = 0.0$ and the flexible closed-shell character bonds for $\mathbb{K} = 1.0$. In other words, in the directional interpretation, the chemical bonding acquires a *range* of values between $\mathbb{K} = 1.0$ (weak, closed-shell *BCP* character) and $\mathbb{K} = 0.0$ (strong, shared-shell *BCP* character)

We found that in all cases there was a greater response of the precessions \mathbb{K} to the unchirped and chirped laser irradiation than to the static E-field, despite the magnitude of the E-field being an order of magnitude greater than that of the laser. The response in terms of the precession \mathbb{K} for the unchirped laser pulse corresponding to the least desirable outcome, i.e. a positive energy gap $\Delta E(S_1-T_1) > 0$, mostly yielded distinctly ordered and separated S_1 and T_1 states. The regions of positive energy gap $\Delta E(S_1-T_1) > 0$ where the chirped pulse had been applied, corresponded to very disordered S_1 and T_1 plots of the precession \mathbb{K} , similar to the desired outcome of the negative energy gap $\Delta E(S_1-T_1) < 0$. The application of the chirped pulse to negative energy gaps $\Delta E(S_1-T_1) < 0$ gave rise to more compact groupings of the S_1 and T_1 plots of the precession K. The chirped pulse overall led to more frequent instances of the desired outcome of a negative energy gap $\Delta E(S_1-T_1) < 0$ within the 100 fs duration, indicating its use in future as a tool to yield the desired negative energy gaps $\Delta E(S_1-T_1) < 0$. Future investigations could therefore focus on engineering the shape of the chirped laser pulse to produce a higher rate of induced negative singlet-triplet gaps.

Acknowledgements

The National Natural Science Foundation of China is acknowledged, project approval number: 21673071. The One Hundred Talents Foundation of Hunan Province are gratefully acknowledged for the support of S.J. and S.R.K. Piotr de Silva is thanked for providing the initial RI-CISD geometry optimized structures and wavefunctions.

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