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Exploring the Excited-State Nonadiabatic Effects in the Semisaturated Planar Tetracoordinated Carbon Molecule C₇H₄

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Abstract: We theoretically study the nonadiabatic relaxation dynamics of low-lying singlet excited-states of semisaturated planar tetracoordinated carbon molecule, C₇H₄. This molecule possesses a stable C_{2v} ground-state equilibrium geometry. The three low-lying singlet states, S₁, S₂ and S₃, lie in the energy gap of about 1.2 eV. The potential energy surfaces constructed within the quadratic vibronic coupling formalism reveal multiple conical intersections in the Franck-Condon region. Upon photoexcitation to S₃, the wavepacket decays rapidly to lower states via these conical intersections. We also observe the wavepacket transfer to S₃ during the initial wavepacket evolution on lower states, suggesting the nonadiabatic behavior of photoexcited planar C₇H₄.

Keywords: excited-states; nonadiabatic dynamics; relaxation pathways



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1. Introduction

The ongoing research in planar tetracoordinated carbon (ptC) for over five decades has opened a new era in the chemistry of carbon. Molecules containing ptC or even higher coordination have been successfully suggested and synthesized. The deviation from the long-established concept of tetrahedral tetracoordinate carbon by van't Hoff [1] and Le Bel [2] has raised the curiosity of researchers. Designing systems containing a planar tetracoordinated carbon center has remained a challenging task. The lone pair of electrons on the central ptC and the electron-deficient 3-centered 2-electron bonds make ptC unstable. The concept of ptC was first introduced by Monkhorst in 1968 [3]. Subsequently, using a planar methane model, Hoffmann and coworkers proposed strategies for stabilizing planar tetracoordinated carbon arrangements by electronic effects as well as steric effects [4,5].

Using those strategies, a number of molecules were proposed theoretically [6–16], though only a few were identified in the laboratory [17–21]. Merino and coworkers have reported a series of semisaturated ptC candidates containing cyclic hydrocarbons, which were created by combining C₅^{2−} moiety with saturated hydrocarbon fragments [22]. These were the first semisaturated cycles, containing a ptC stabilized only by electronic factors. The authors analyzed various ground-state properties, and they inferred that the multicentric nature of the bonding within the C₅^{2−} skeleton and the resulting electron delocalization provides stability to these molecules.

Although several studies have focussed on the various ground-state properties of ptCs, the excited-state properties of these molecules remain unexplored. In the present work, we focus on elucidating the excited-state dynamics of the semisaturated ptC, C₇H₄ (tricyclo[4.1.0.0^{1,3}]hept-2,6-diene-2,7-diyl) (cf., Figure 1), using combined electronic structure computations and quantum dynamics simulations. We generate the potential energy surfaces (PESs) of low-lying singlet excited electronic states within the quadratic vibronic coupling (QVC) framework. Subsequently, we perform quantum-mechanical wavepacket simulations within the well-established multidimensional configurational time-dependent Hartree (MCTDH) method. Finally, we analyze the electronic populations and reduced

nuclear densities and various stationary points of PESs to gain insights into the excited-state relaxation decay channels of the ptC molecule, C_7H_4 .

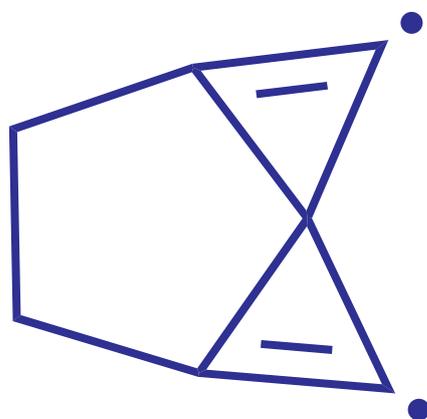


Figure 1. Structure of C_7H_4 .

2. Theoretical Framework

2.1. Electronic Structure Calculations

We perform the optimization and frequency computations associated with the ground-state equilibrium geometry of C_7H_4 within the density functional theory (DFT) using gas-phase conditions. These computations use the B3LYP [23]/6-311++G(d,p) level of theory. For excited-state computations, we rely on the time-dependent variant of DFT (TDDFT). We obtain vertical excitation energies and corresponding oscillator strengths using the long-range corrected ω B97XD functional (0.22 HF at short-range and 1.00 HF at long-range) [24] in combination with 6-311++G(d,p) basis set. All the calculations are done using Gaussian 16 program package [25].

To verify the suitability of the selected functional, we have done benchmarking calculations of excited-states with various quantum chemical methods. Accordingly, we employ time-dependent variants of B3LYP (containing 0.20 Hartree–Fock (HF) exchange), CAM-B3LYP [26] (comprises of 0.19 HF exchange at short-range, and 0.65 HF at long-range), LC- ω PBE [27] (no HF exchange at short-range and 1.00 HF at long-range) and M06-2X (comprises of 0.54 HF exchange) [28]. We use the 6-311++G(d,p) basis set for these computations. Further, we also evaluate excited-state energies using post-HF methods: equation of motion coupled cluster with single and double excitations (EOM-CCSD) method [29,30], resolution-of-the-identity second-order approximate coupled-cluster singles and doubles (RI-CC2) method [31], and algebraic diagrammatic construction method to second-order (ADC(2)) method [32]. These computations use the correlation consistent polarized valence double zeta (cc-pVDZ) basis set. The geometry optimized at the B3LYP/6-311++G(d,p) level of theory was used for all the above computations. We employ Gaussian 16 software package for TDDFT and EOM-CCSD computations and TURBOMOLE 7.4 software [33] for ADC(2) and RI-CC2 computations.

2.2. Vibronic Hamiltonian

Based on the computed vertical excitation energies, we are interested in studying the excited-state dynamics of the first three singlet excited-states of C_7H_4 . For this, we construct a 3×3 vibronic Hamiltonian based on the well-established QVC approach [34]. The Hamiltonian can be expressed as :

$$\mathcal{H} = (T_N + V_0)\mathbf{1}_3 + \begin{pmatrix} E_{S_1}^0 + \sum_{i \in a_1} \kappa_i^{(S_1)} Q_i + \frac{1}{2} \sum_{i \in a_1} \gamma_i^{(S_1)} Q_i^2 & \sum_{i \in a_1} \lambda_i^{(S_1-S_2)} Q_i & \sum_{j \in a_2} \lambda_j^{(S_1-S_3)} Q_j \\ h.c. & E_{S_2}^0 + \sum_{i \in a_1} \kappa_i^{(S_2)} Q_i + \frac{1}{2} \sum_{i \in a_1} \gamma_i^{(S_2)} Q_i^2 & \sum_{j \in a_2} \lambda_j^{(S_2-S_3)} Q_j \\ & & E_{S_3}^0 + \sum_{i \in a_1} \kappa_i^{(S_3)} Q_i + \frac{1}{2} \sum_{i \in a_1} \gamma_i^{(S_3)} Q_i^2 \end{pmatrix} \quad (1)$$

Here, T_N and V_0 are the ground-state kinetic energy and potential energy operators and are expressed in terms of the dimensionless normal coordinate (Q) within the harmonic approximation. E_m^0 represents the vertical excitation energy of the excited-states (for S_m , $m = 1, 2$ and 3). κ_i and γ_i denotes the linear and quadratic intrastate coupling parameters, respectively, along the totally symmetric vibrational mode, i . λ_j is the interstate coupling parameter along the non-totally symmetric vibrational mode, j . The interstate coupling constants between states of same symmetry (S_1 and S_2) are computed along the totally symmetric vibrational mode, a_1 , and is represented as λ_i . These coupling parameters are evaluated using the following expressions:

$$\kappa^{(S_m)} = \frac{\partial V_{S_m}}{\partial Q_i} \Big|_{Q_0}, \quad i \in a_1 \quad (2)$$

$$\gamma^{(S_m)} = \frac{\partial^2 V_{S_m}}{\partial Q_i^2} \Big|_{Q_0}, \quad i \in a_1 \quad (3)$$

$$\lambda_{i/j}^{(S_m-S_n)} = \left[\frac{1}{8} \frac{\partial^2}{\partial Q_{i/j}^2} |V_{S_m}(Q) - V_{S_n}(Q)|^2 \right]_{Q_0}^{1/2}, \quad i \in a_1; j \in a_2 \quad (4)$$

where, V_{S_m} and V_{S_n} are the adiabatic potential energies of two different electronic states, S_n and S_m , respectively; Q_0 represents the ground-state equilibrium geometry of the molecule.

2.3. Dynamics Simulations

We simulate the quantum nuclear dynamics of the singlet excited-states of C_7H_4 by using multiconfiguration time-dependent Hartree (MCTDH) approach [35–37] which is designed to solve the time-dependent Schrodinger equation for multidimensional dynamical systems. In this method, the nuclear wavefunction, Ψ , of a system with f degrees of freedom (DOF) is expressed as:

$$\Psi(Q_1, \dots, Q_f, t) = \sum_{i_1=1}^{n_1} \dots \sum_{i_f=1}^{n_f} R_{i_1, \dots, i_f}(t) \prod_{k=1}^f \phi_{i_k}^{(k)}(Q_k, t). \quad (5)$$

where Q_1, \dots, Q_f are the nuclear coordinates of vibrational modes. R_{i_1, \dots, i_f} and $\phi_{i_k}^{(k)}$ denote the MCTDH expansion coefficients and single-particle functions (SPFs), respectively. n_k represents the number of SPFs to describe the k -th DOF.

To reduce the memory requirement of the above treatment, we adopt a “mode combination” technique in which SPFs that can describe a set of DOF are used. The nuclear wavefunction can be then rewritten as a multi-configuration over p generalized particles :

$$\Psi(Q'_1, Q'_2, \dots, Q'_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_p=1}^{n_p} R_{j_1, \dots, j_p}(t) \phi_{j_1}^{(1)}(Q'_1, t), \dots, \phi_{j_p}^{(p)}(Q'_p, t) \quad (6)$$

with

$$\phi_j^{(k)}(Q'_k, t) = \phi_j^{(k)}(Q_1, Q_2, \dots, Q_w, t) \quad (7)$$

where $Q'_k = (Q_1, Q_2, \dots, Q_w)$ represents the multidimensional coordinate for mode k .

Out of the 28 degrees of freedom (27 vibrational modes and a set of electronic states) of C_7H_4 , a total of 14 (9 a_1 and 5 a_2) modes were selected based on the excitation strength of

the modes. It is to be noted that S_1 – S_3 and S_2 – S_3 couplings are along a_2 modes and coupling between S_1 and S_2 , belonging to the same symmetry, are along a_1 modes. The nuclear wavepacket generated on S_3 PES has been propagated for 300 fs with a time step of 1 fs. The diabatic electronic populations and nuclear densities are then extracted to study the internal conversion dynamics. The Heidelberg MCTDH code version 8.5 Revision 11 [38] is employed for these calculations. Details of MCTDH dynamics such as mode combination, primitive basis, and SPFs are given in Supplementary Information.

3. Results and Discussion

3.1. PESs and Conical Intersections

We collect the vertical excitation energies, oscillator strengths and symmetries of low-lying singlet excited-states of C_7H_4 computed at different levels of theory in Table 1. All computational methods yield the same electronic symmetries for S_1 and S_2 . We also note that all methods predict B_2 symmetry for S_3 except TD-B3LYP and TD-M06-2X. The latter two methods show A_1 symmetry for this state. Concerning oscillator strengths, all methods predict a smaller value for S_1 than higher electronic states. Here, the important feature of Table 1 is the S_1 – S_3 energy gap; all methods predict a gap of about 1.2 eV. As these states lie within this energy gap, one would expect the molecule to follow nonadiabatic behavior upon photoexcitation. As the vertical energies (as well as the oscillator strengths) of the excited-states computed at the ω B97XD/6-311++G(d,p) level of theory match well with the computationally expensive wavefunction methods, we perform all calculations using this method.

Table 1. Vertical excitation energies of C_7H_4 computed using different levels of theory. 6-311++G(d,p) is the basis set used for the TDDFT methods and cc-pVDZ is used for the wavefunction based methods.

Methods	S_1	S_2	S_3
TD- ω B97XD	4.3417 (B_1 , 0.001)	4.8192 (B_1 , 0.043)	5.5606 (B_2 , 0.049)
TD-B3LYP	4.0221 (B_1 , 0.005)	4.5325 (B_1 , 0.032)	5.0136 (A_1 , 0.010)
TD-CAMB3LYP	4.3389 (B_1 , 0.001)	4.7960 (B_1 , 0.045)	5.5310 (B_2 , 0.045)
TD-LC- ω PBE	4.5102 (B_1 , 0.000)	4.9985 (B_1 , 0.050)	5.7237 (B_2 , 0.037)
TD-M06-2X	4.2035 (B_1 , 0.000)	4.5731 (B_1 , 0.039)	5.4983 (A_1 , 0.004)
EOM-CCSD	4.3121 (B_1 , 0.002)	4.9658 (B_1 , 0.032)	5.5197 (B_2 , 0.031)
ADC(2)	4.3239 (B_1 , 0.003)	4.9202 (B_1 , 0.030)	5.4091 (B_2 , 0.042)
RICC2	4.2634 (B_1 , 0.004)	4.8697 (B_1 , 0.027)	5.3844 (B_2 , 0.046)

To explore the nuclear dependence of these electronic states, we plot adiabatic potential energy profiles (solid lines) against in-plane ring deformation vibrational coordinates (Q_{15}) in Figure 2. The ab initio energies (plus harmonic potential) are shown as filled circles in this figure. We observe that the potential energy profiles generated within the QVC approach reproduce the ab initio energies quite well, confirming the suitability of the latter approach to study the dynamics happening within the Franck-Condon (FC) region. We observe multiple curve crossings between the excited- states of interest. Such crossings also occur in the other vibrational coordinate space, however those data are not shown here for brevity. It should be mentioned that these crossings would form the seam of conical intersection in the multidimensional space. Figure 3 depicts the conical intersections associated with the adiabatic PESs of S_1 , S_2 , and S_3 states along the coordinates of ring deformation (Q_{15}) and C=C stretch (Q_{22}) vibrations. These vibrational modes are represented in Figure 4.

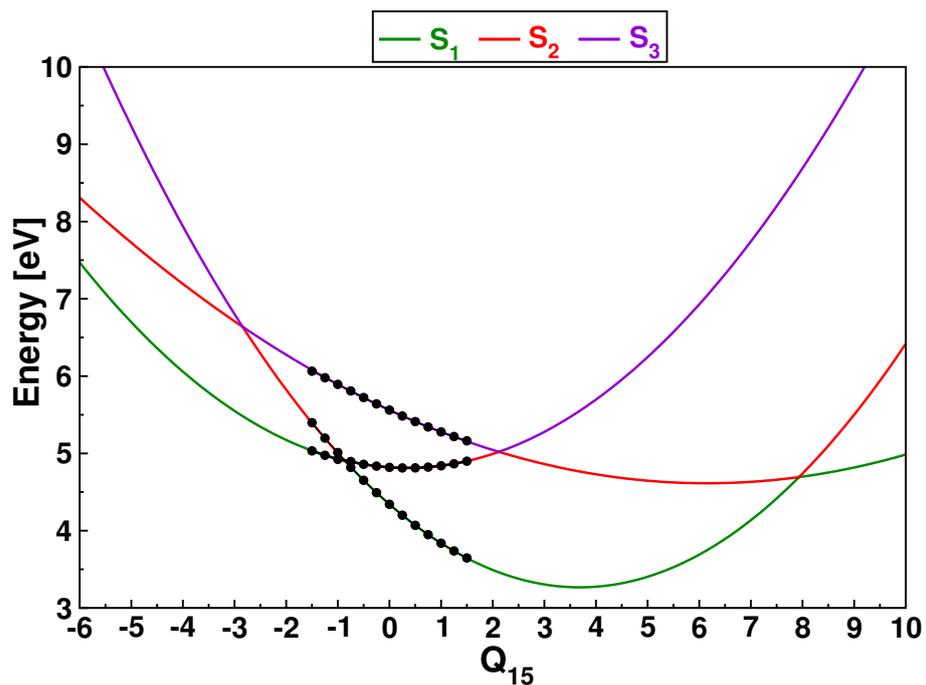


Figure 2. Computed adiabatic potential energy curves of along Q_{15} of C_7H_4 within the QVC approach. The solid circles represent the ab initio points plus ground-state harmonic potential energy.

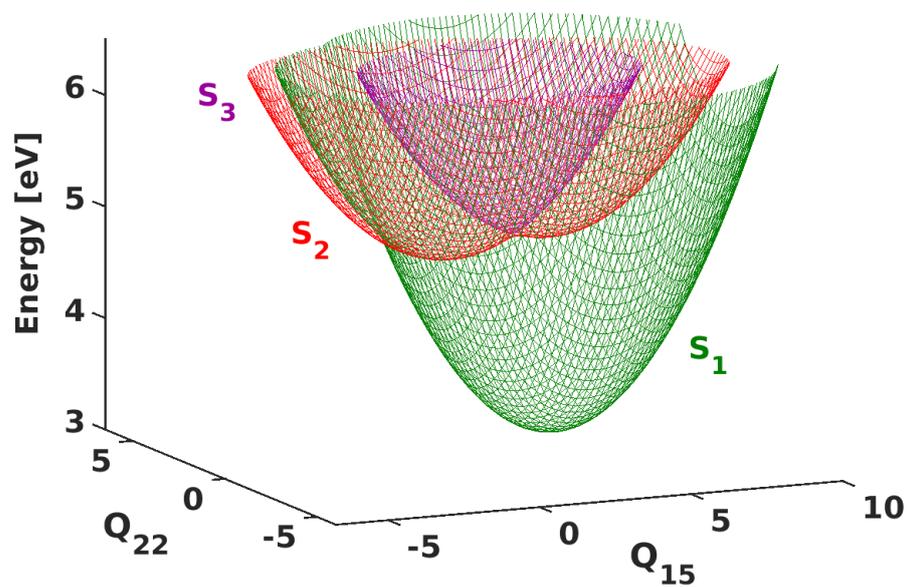


Figure 3. Adiabatic potential energy surfaces of C_7H_4 in the Q_{15} and Q_{22} vibrational space computed within the QVC approach.

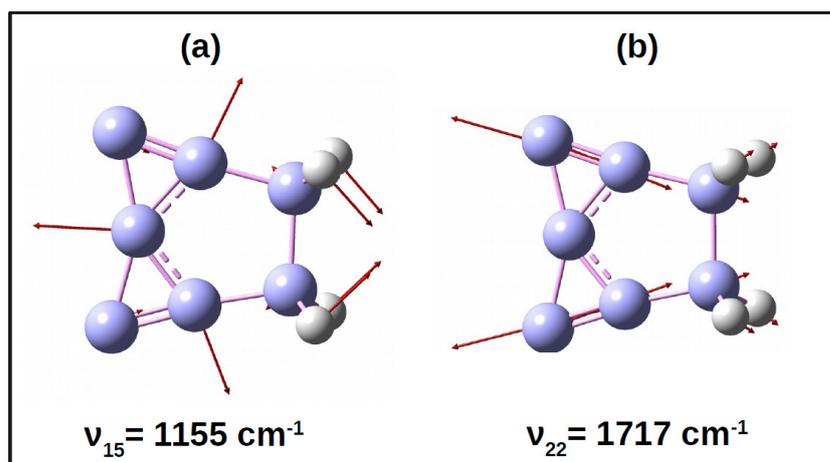


Figure 4. Schematic representation of the (a) in-plane ring deformation (Q_{15}) and (b) C=C stretch (Q_{22}) vibrational modes of C_7H_4 . Harmonic frequencies obtained using B3LYP/6-311++G(d,p) level of theory are also shown.

We also evaluate two other important quantities: minimum energy conical intersection and equilibrium minimum of excited-states. These quantities are crucial to explain the wavepacket dynamics happening on the coupled S_1 – S_2 – S_3 PESs. Following expressions are employed to evaluate those quantities: [39]

$$MECI = a + \frac{(b - c)^2}{2d} - \frac{1}{2} \sum_{i=1}^N \frac{\sigma_i^2}{\omega_i} \quad (8)$$

where,

$$a = \frac{E_1^0 + E_2^0}{2} \quad (9)$$

$$c = \frac{E_2^0 - E_1^0}{2} \quad (10)$$

$$b = \sum_{i=1}^N \frac{\delta_i \sigma_i}{\omega_i} \quad (11)$$

$$d = \sum_{i=1}^N \frac{\delta_i^2}{\omega_i} \quad (12)$$

$$\sigma_i = \frac{\kappa_i^{(2)} + \kappa_i^{(1)}}{2} \quad (13)$$

$$\delta_i = \frac{\kappa_i^{(2)} - \kappa_i^{(1)}}{2} \quad (14)$$

$$E_m^{\min} = E_m^0 - \frac{1}{2} \sum_{i=1}^N \frac{\kappa_i^2}{\omega_i} \quad (15)$$

where ω_i is the harmonic frequency of the i th totally symmetric vibrational mode and N is the total number of such modes.

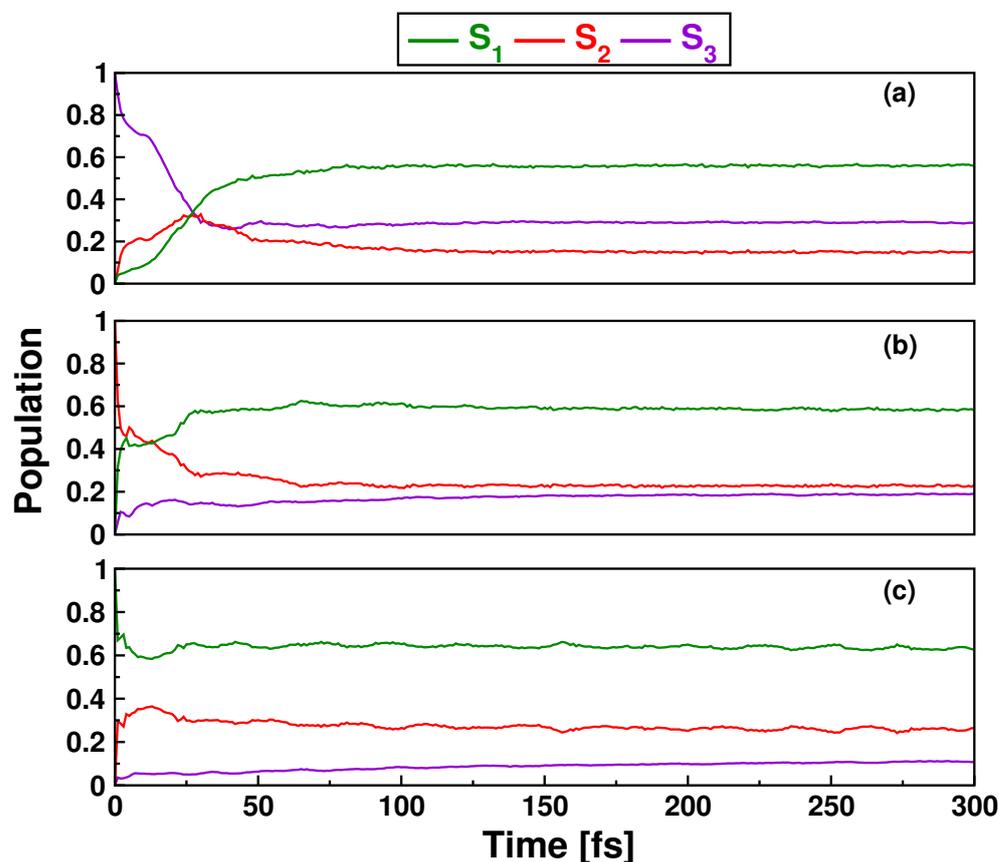
The molecule might display unexpected nonradiative decay dynamics due to the presence of accessible conical intersections within the FC region (cf., Table 2). For instance, the S_2 – S_3 conical intersection lies ~ 0.5 eV below the FC point of S_3 (cf., Tables 1 and 2). Hence, upon excitation to S_3 , the molecule can, in principle, decay rapidly via this conical intersection. We expect this intersection point and the S_1 – S_3 conical intersection, that lies slightly above (~ 0.1 eV) the FC point of S_3 , might play an important role in the decay dynamics.

Table 2. Relevant stationary points (state minima and MECI) on the coupled S_1 – S_2 – S_3 PESs of C_7H_4 .

Stationary Point	Energy (eV)
S_1^{\min}	3.6039
S_2^{\min}	4.7940
S_3^{\min}	4.3006
S_1/S_2	4.7970
S_1/S_3	5.6376
S_2/S_3	5.0552

3.2. Singlet Dynamics

To investigate the fate of C_7H_4 in the higher excited singlet states, we perform dynamics simulations by launching the initial wavepacket at the FC point of the “bright” S_3 . Figure 5a collects the time-dependent electronic population profiles obtained from this wavepacket propagation calculation. We observe a rapid population transfer from S_3 to S_2 . The wavepacket evolving on S_3 could easily access the S_2/S_3 MECI (~ 5.06 eV, cf., Table 2) and thus promote rapid nonadiabatic population transfer.

**Figure 5.** Diabatic electronic population profiles of singlet excited-states generated by propagation of initial wavepacket on (a) S_3 , (b) S_2 , and (c) S_1 of C_7H_4 .

We note that $\sim 70\%$ depopulation of S_3 happens within the first 40 fs of propagation time. We observe a sharp rise in the S_1 population during this period. This sharp rise would emerge from the wavepacket decay via S_1 – S_3 and S_1 – S_2 conical intersections. Interestingly, the populations of the involved states remain almost unchanged after 50 fs. These observations suggest the remnant wavepacket localization at the respective equilibrium minimum of involved electronic states after the early nonadiabatic wavepacket transfer.

To further validate the nonadiabatic population transfer, we plot the reduced nuclear densities associated with the ring deformation mode, i.e., Q_{15} , for three electronic states in

Figure 6. The density would be maximum on S_3 at $t=0$ fs as the wavepacket propagation starts on this state. We observe the rapid density reduction within 20 fs, and after that, the density remains unchanged until the end of propagation time. For S_2 , the density accumulates rapidly after a few femtoseconds and reaches a maximum at about 20 fs. After that, the density reduces up to 50 fs and remains unchanged till 300 fs. For S_1 , we observe a gradual increase of nuclear density, reaching a maximum value at about 20 fs. After that, the nuclear density on S_1 would remain unchanged up to 300 fs. From these observations, we infer that the wavepacket decay to S_1 would occur within a few tens of femtoseconds after photoexcitation to S_3 .

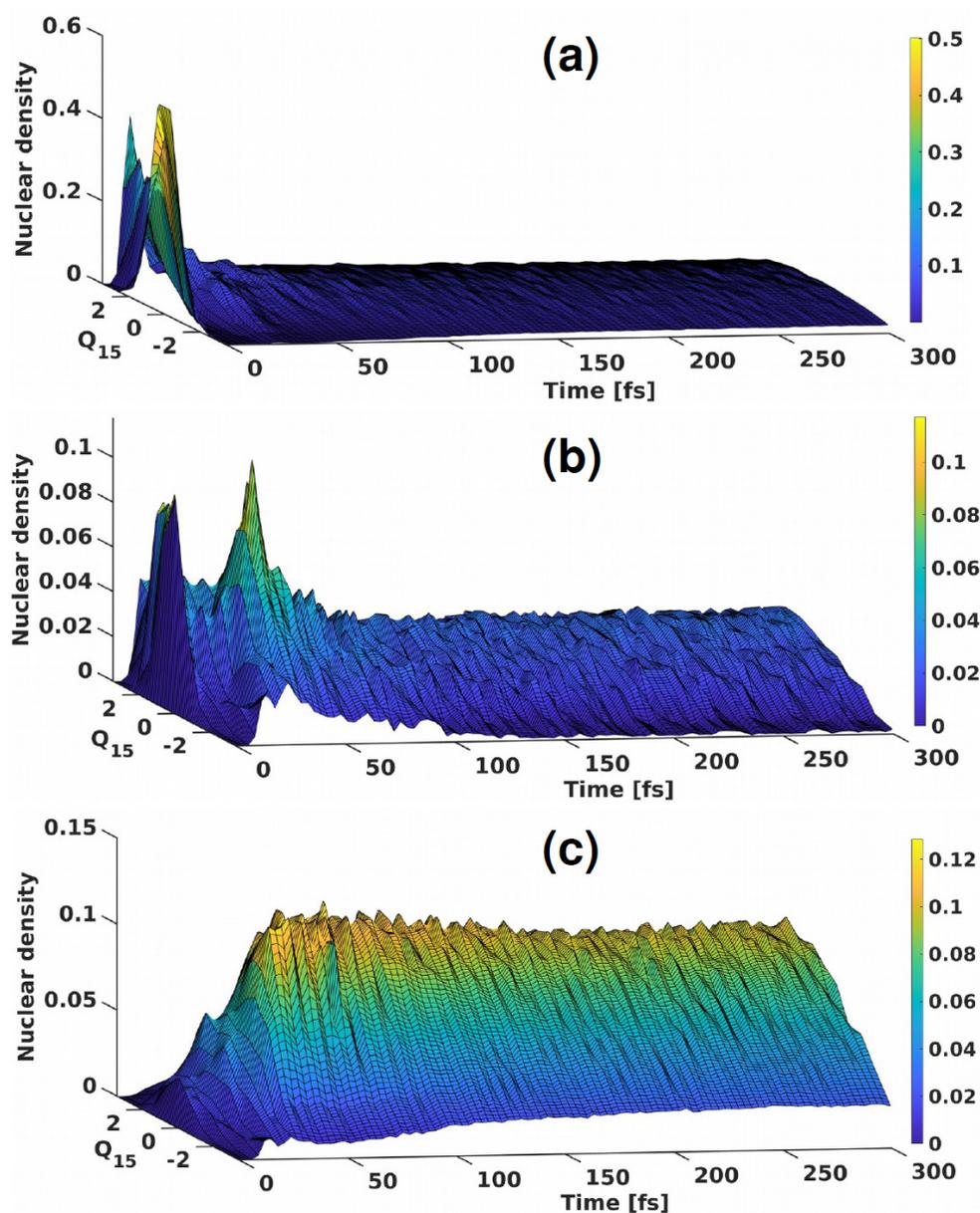


Figure 6. Nuclear densities variation of (a) S_3 , (b) S_2 , and (c) S_1 along Q_{15} of C_7H_4 , obtained by propagating initial wavepacket on the “bright” S_3 state.

Next, we launch the initial wavepacket at the FC point of S_2 and S_1 to explore the decay dynamics of individual electronic states. The accessible S_1/S_2 MECI (~ 4.80 eV, cf., Table 2) combined with the high interstate coupling via a_1 modes results in an extremely rapid population transfer from S_2 to S_1 (cf., Figure 5b). The S_1 population reaches an

asymptotic value of ~ 0.6 at the end of 300 fs. A minor population transfer to S_3 can also be seen, attributed to the strong nonadiabatic coupling between S_2 and S_3 states.

The wavepacket propagated on the S_1 PES shows an appreciable decay ($\sim 40\%$) to S_2 till the initial 20 fs and further, remains constant (cf., Figure 5c). Such population profile suggests that the molecule might be trapped at the equilibrium minimum of S_1 , which is ~ 0.7 eV lower in energy from the S_1 FC point. The molecule could no longer access any conical intersections, resulting in no noticeable population transfer. Similar profile is also observed in the variation of nuclear densities (along Q_{15} vibrational mode) across the excited-states with the wavepacket evolving on S_1 (cf., SM8 in Supplementary Information). It is noted that no state shows 100% decay within 300 fs. So dynamics simulations need to be conducted for a longer duration for the complete decay of the excited-states.

We note that the QVC model employed in this study would be helpful to gain insights into the FC dynamics. However, concerning the fluxional behavior of molecules containing ptC, it is necessary to adopt a theoretical model that involves possible excited-state dissociation pathways. Identifying such dissociative pathways through experimental investigations can be complicated due to nonadiabatic events occurring in the FC region. However, one could rely on the high-level on-the-fly dynamics simulations to study the photoproducts of ptC molecules.

4. Conclusions

In the present work, we provide vital insights on the nonadiabatic relaxation dynamics of the semisaturated ptC molecule, C_7H_4 . PESs constructed by employing QVC formalism revealed multiple conical intersections among the three singlet excited-states, S_1 , S_2 , and S_3 . The molecule excited to the optically “bright” S_3 returns to S_1 on an ultrafast timescale via these conical intersections. Similarly, these crossing points also promote the wavepacket transfer to higher states (S_2 and S_3) while the wavepacket is initially on S_1 , demonstrating the nonadiabatic behavior of C_7H_4 irrespective of excitation energy. Although the present study has provided essential features of excited-state decay dynamics, a detailed quantum dynamics study using the multi-reference configuration interaction (MRCI) or multiconfigurational quasidegenerate perturbation theory (MCQDPT) PESs is planned to provide an accurate picture of the relaxation pathways of C_7H_4 .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atoms10010010/s1>. Optimized ground-state geometries, harmonic frequencies, vibronic coupling parameters, MCTDH details and nuclear density plots are given.

Author Contributions: Conceptualization, S.R.V.; methodology, S.R.V.; validation, S.R.V.; formal analysis, C.M.J., P.N. and S.V.K.I.; investigation, C.M.J., P.N. and S.V.K.I.; data curation, C.M.J., P.N. and S.V.K.I.; writing—original draft preparation, C.M.J.; writing—review and editing, S.R.V.; supervision, S.R.V. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ptC	Planar tetracoordinated carbon
PES	Potential energy surface
QVC	Quadratic vibronic coupling
MCTDH	Multiconfiguration time-dependent hartree
TDDFT	Time-dependent density functional theory
EOM-CCSD	Equation of motion coupled cluster with single and double excitations
RI-CC2	Resolution-of-the-identity second-order approximate coupled-cluster singles and doubles
ADC(2)	Algebraic diagrammatic construction method to second-order
FC	Franck-Condon
MECI	Minimum energy conical intersection

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