Topological Effects in Vibronically Coupled Degenerate Electronic States: A Case Study on Nitrate and Benzene Radical Cation

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ABSTRACT: We carry out detailed investigation for topological effects of two molecular systems, NO3 radical and C6H5+ (Bz+) radical cation, where the dressed adiabatic, dressed diabatic, and adiabatic-to-dressed diabatic potential energy curves (PECs) are generated employing ab initio calculated adiabatic and diabatic potential energy surfaces (PESs). We have implemented beyond Born–Oppenheimer (BBO) theory for constructing smooth, single-valued, and continuous diabatic PESs for five coupled electronic states [J. Phys. Chem. A 2017, 121, 6314–6326]. In the case of NO3 radical, the nonadiabatic coupling terms (NACTs) among the low-lying five electronic states, namely, X̃A2 (1B2g), Ã2E′ (1A1g and 1B2g), and B̃E′ (1A1g and 2B2g), bear the signature of Jahn–Teller (JT) interactions, pseudo JT (PJT) interactions, and accidental conical intersections (CIs). Similarly, Bz+ radical cation also exhibits JT, PJT, and accidental CIs in the interested domain of nuclear configuration space. In order to generate dressed PECs, two components of degenerate in-plane asymmetric stretching modes are selectively chosen for both the molecular species (Qx=Qy pair for NO3 radical and Qx=Qy pair for Bz+ radical cation). The JT coupling between the electronic states is essentially originated through the asymmetric stretching normal mode pair, where the coupling elements exhibit symmetric and nonlinear functional behavior along Qx and Qy, normal modes.

1. INTRODUCTION
The Born–Oppenheimer (BO) approximation1,2 completely decouples the mechanics of fast-moving electrons and slow-moving nuclei, leading to satisfactory explanation of several experimental findings. On the contrary, complete or partial failure of this theoretical framework could be encountered for excited-state molecular processes such as charge-transfer reactions, measurements of scattering cross sections, and photochemical reactions.3,4 In such phenomena, the non-negligible electron–nuclear coupling designated as nonadiabatic coupling terms (NACTs) not only plays a significant role for this discrepancy but also attains singular characteristics at degenerate points in the nuclear configuration space (CS). Therefore, overlooking of NACTs5,6 one of the major outcomes of BO treatment often leads to erroneous dynamical results and inaccurate numerical data regarding the molecular processes.

In the early sixties, Longuet-Higgins noticed multivaluedness of the eigenfunctions7 while traversing along a closed path encircling a point of conical intersection (CI). Though this unusual behavior was circumvented by incorporating a phase factor8 in an ad hoc manner, Mead and Truhlar9 eliminated this multivaluedness behavior of wavefunctions by encompassing a vector potential into the nuclear Hamiltonian. On the other hand, the Hellmann–Feynman theorem predicts the possibility of singularity in NACTs10,11 over the nuclear CS whenever electronic states appear to be degenerate or near degenerate. This singular characteristics can be removed by transforming to a different representation or basis, known as the diabatic representation where the singular kinetic coupling terms are converted into smoothly varying off-diagonal terms in the diabatic potential energy matrix. Such unitary transformation is known as the adiabatic-to-diabatic transformation (ADT). In this context, it may be noted that vector field created by the NACTs can be decomposed into longitudinal and transverse components, where the former is expressed as the derivative of a scalar and the latter by the curl of a vector. By performing ADT, the longitudinal component (the removable part) can be eliminated,5,12 whereas the transverse or the nonremovable part may be neglected at the close vicinity of a CI.

Hobey and McLachlan devised the first technique of ADT only for one degree of freedom and latter on, F. T. Smith implemented this method for a diatomic molecule. M. Baer proposed a general formalism for the diabatization of two coupled adiabatic potential energy surfaces (PESs) involved on the process of triatomic collision. In that work, the ADT condition is depicted which is the key mechanistic element for the determination of the ADT matrix elements by integrating the differential equations along a two-dimensional contour over the nuclear CS.5,12 On the other hand, only the fulfillment of “curl condition”12,13 guarantees the existence and the uniqueness of the solution to those equations. Generally, ADT angles can be calculated by integrating the NACTs around the
CI point(s) and because of the quantized nature of the closed contour integrals, resulting angles will attain magnitudes in multiples of \( \pi \) (pi). The satisfaction of aforementioned curl conditions also validates the presence of a set of electronic states forming a complete space. Though the above said condition is invalid at the degenerate CI point(s), nevertheless, the singular NACTs can be taken out from the SE if the line integrals exhibit quantization within the sub-Hilbert space constituted with all coupled electronic states.32 The beyond BO (BBO) treatment for three, four, and five coupled electronic states in terms of electronic basis functions or the ADT matrix elements has been generalized by Adhikari et al.16–19 and the explicit expressions of the NACTs, curl–divergence equations, curl conditions, and the diabatic PESs have also been formulated in terms of the ADT angles. Moreover, this theoretical development has been successfully employed on model16–18,20 as well as realistic15,21–24 systems for constructing smooth, continuous, and single-valued diabatic PESs. Molecular systems having strong vibronic interactions between five electronic states are omnipresent in nature. NO3 radical and C6H6 + (Bz+) radical cation are two highly intricate examples of five electronic state sub-Hilbert spaces. Recently, we have pursued formulation of BBO equations for five state sub-Hilbert spaces, devised the ADT equations and explicit expressions of NACTs in terms of ADT angles, and successfully implemented the formalism for NO3 radical and Bz+ radical cation.

In this article, our aim is to generate dressed adiabatic potential energy curves (PECs), dressed diabatic PECs, and adiabatic PECs via dressed diabatic potentials in a pair of normal mode coordinates for both the molecular/ionic species. The PECs carry the signature of topological effects in their functional variation along a particular normal mode coordinate by taking average over the other normal mode coordinate. Symmetric variation of dressed diabatic couplings indicates the absence of linear and higher odd order functions in electron–nuclear couplings, whereas asymmetric diabatic couplings incorporate both odd and even order polynomials in their functional forms. Detailed topological studies clearly reveal effects of NACTs in stabilization or destabilization of PESs.

NO3 radical is one of the most challenging molecular species in the realm of nonadiabatic dynamics. It exhibits highly complex spectral features due to intense vibronic coupling between its low-lying five electronic states \( \tilde{X}^2A_1 \) (\( 1^2B_2 \)), \( \tilde{A}^2E' \) (\( 1^2A_2 \) and \( 2^2B_2 \)), and \( \tilde{B}^2E' \) (\( 1^2A_1 \) and \( 2^2D_2 \)) in the Franck–Condon region of nuclear CS. Several theoretical predictions were already proposed to elucidate the underlying principle of the complex spectral envelop, obtained from various experimental tools such as dispersed fluorescence spectroscopy,25,26 Fourier transform infrared spectroscopy,27,28 photoelectron spectroscopy,29 and also from cavity ringdown spectroscopy.30,31 In spite of various controversies about the ground state equilibrium geometry, Eisfeld and Morokuma32 finally confirmed the radical to be of \( D_{2h} \) symmetry. Mayer et al.,33 Faraji et al.,34 and Stanton et al.35,36 also promised some theoretical development to reveal the key features of the experimentally obtained spectral profile. It is noteworthy to mention that strong Jahn–Teller (JT) interactions prevail within the \( \tilde{A}^2E' \) and \( \tilde{B}^2E' \) states at the equilibrium \( D_{2h} \) point along with several accidental CIs at \( C_{2v} \) geometries.19,37 In addition, the ground state, \( \tilde{X}^2A_1 \) experiences strong pseudo JT (PJT) interaction due to the \( \tilde{B}^2E' \) state.19,37 These vibronic phenomena strongly influence the nuclear dynamics and the associated features of the photoelectron spectra26,38 of the NO3− anion.

The photophysics of Bz+ radical cation is one of the center of attraction in the arena of BBO theory. In all theoretical developments,39–47 the electronic states, namely, \( \tilde{X}^2E_{1u} \), \( \tilde{B}^2E_{2g} \), \( \tilde{C}^2A_{2u} \), \( \tilde{D}^2E_{1u} \), and \( \tilde{E}^2B_{2u} \) along with the CIs among the PESs were investigated for its dynamical studies. Goode et al.38 pointed out the complex vibrational pattern of \( \tilde{B}^2E_{2g} \) state using the combined effect of Herzberg–Teller and PJT coupling between this state and close-lying \( \tilde{C}^2A_{2u} \) state. JT coupling parameters for \( e_{2g} \) vibrational modes of this radical cation which are used to illustrate the photoinduced Rydberg ionization spectra of the \( \tilde{B}^2E_{2g} \) state49 were extensively measured by Johnson.50 The low-lying doublet states of Bz+, \( \tilde{B}^2E_{2g} \), and \( \tilde{C}^2A_{2u} \) show intense nonadiabatic interactions among them. The JT effects within the ground, \( \tilde{X}^2E_{1g} \) as well as the excited state, \( \tilde{B}^2E_{2g} \) are quite predominant particularly lowering the symmetry of ground state equilibrium structure of Bz+ to \( D_{2h} \). Apart from the JT effects, there are accidental CIs and PJT interactions prevailing between \( \tilde{B}^2E_{2g} \) and \( \tilde{C}^2A_{2u} \) states.39 We have investigated the JT interactions of the ground (\( \tilde{X}^2E_{1g} \)) and excited states (\( \tilde{B}^2E_{2g} \)) as well as accidental CIs within the higher excited states (\( \tilde{B}^2E_{2g} \)–\( \tilde{C}^2A_{2u} \)) using the ADT equations by employing the BBO formalism.39

The article is arranged as follows: Section 2 presents detailed theoretical framework of BBO theory for a five electronic state sub-Hilbert spaces. This section also gives a brief description of the underlying equations for calculating dressed potentials. In Section 3, we explore topological effects prevailing in both of the molecular systems. This detailed investigation will be highly useful to predict the possible functional forms of the inherent nonadiabatic couplings. Finally, the summary of this topological study is laid out in Section 4.

### 2. BBO THEORY AND DIABATIC HAMILTONIAN

As per the BO treatment, total molecular wavefunction can be expanded as a linear combination of the electronic wavefunctions where the combining coefficients represent the nuclear counterpart. While considering a sub-Hilbert space of finite dimension, a total electron–nuclei wavefunction takes the following form

\[
\Psi(s,E_s) = \sum_{i=1}^{n} \psi(s,E_s)|\xi(s,E_s)\rangle
\]

(1)

This wavefunction is the eigenfunction of molecular SE, and the corresponding eigenvalue represents the total energy of the system

\[
\hat{H}(s,E_s)|\psi(s,E_s)\rangle = E_s|\psi(s,E_s)\rangle
\]

(2)

The molecular Hamiltonian can be partitioned into a nuclear kinetic energy operator (\( \hat{T}_n \)) and the electronic Hamiltonian (\( \hat{H}_e(s,E_s) \))

\[
\hat{H}(s,E_s) = \hat{T}_n(s,E_s) + \hat{H}_e(s,E_s)
\]

(3)

where the nuclear kinetic energy operator is defined as

\[
\hat{T}_n = -\frac{1}{2} \sum_i \left( \nabla_{s_i}^2 \right) \nabla_{m_i}^2
\]

(4)

On the other hand, electronic wavefunctions (\( |\xi(s,E_s)\rangle \)), that is, the basis of the BO expansion, are eigenfunctions of \( \hat{H}_e(s,E_s) \) operator with a nuclear coordinate-dependent
eigenvalue $u_i(s_j)$. Therefore, the electronic eigenvalue equation is presented as below

$$\hat{H}_e(s_j l_{s_j}) \xi(s_j) = u_i(s_j) \xi(s_j)$$  \hspace{1cm} (5)$$

When the BO expansion of molecular wavefunction is substituted in total Hamiltonian [eq 2] and it is projected with various electronic wavefunctions, the compact adiabatic (kinetically coupled) SE takes the following matrix form

$$\left[ -\frac{1}{2} (\nabla \mathbf{r} + \mathbf{r})^2 + \mathbf{U} - \mathbf{E} \right] \psi = 0$$  \hspace{1cm} (6)$$

where $U_0 = u_i \delta_{ij}$ and $\mathbf{r}$ is the nonadiabatic coupling matrix (NACM) defined as

$$\bar{r}_{ij} = \langle \xi(s_j l_{s_j}) | \mathbf{r} | \xi(s_j l_{s_j}) \rangle$$  \hspace{1cm} (7)$$

The adiabatic representation of the SE is difficult to solve because of the numerical instability of the NACTs at the points of degeneracy. Therefore, we encounter the limitations of the adiabatic representations which exhibit the inevitable necessity of a different representation where the nonadiabatic interactions appear as continuous, smooth, and single-valued diabatic coupling terms. This transformation could be achieved by using an orthogonal rotation matrix ($\mathbf{A}$)

$$\psi = \mathbf{A} \phi^d$$  \hspace{1cm} (8)$$

where $\psi$ and $\phi^d$ symbolize the adiabatic and diabatic nuclear wavefunction, respectively.

While incorporating the aforementioned form of wavefunction, diabatic representation of the nuclear SE takes the following expression

$$-\frac{1}{2} \nabla^2 \phi^d + (\mathbf{W} - \mathbf{E}) \phi^d = 0$$  \hspace{1cm} (9)$$

where

$$\mathbf{W} = \mathbf{A} \mathbf{U} \mathbf{A}$$  \hspace{1cm} (10)$$

under the condition

$$\nabla \mathbf{A} + \mathbf{A} \mathbf{r} = 0$$  \hspace{1cm} (11)$$

known as the ADT condition.

The ADT condition [eq 11] can be used as the precursor of devising the ADT equations. For five (5) electronic state sub-Hilbert spaces, the model ADT matrix can be constructed by multiplying $C_2$ rotation matrices in a particular way. Those could be arranged in $C_2$! different ways, but we carry out the formulation for a particular order of multiplication. On the other hand, anyone of the possible arrangements produces same numerical value of the diabatic potential energy matrices. For any one of the rotation matrices, $\mathbf{A}_i(\theta_i)$, where $ii$ and $jj$ elements become $\cos \theta_i$ and $ij$ and $ji$ elements take the form of $\sin \theta_i$, and $-\sin \theta_i$, respectively. Among the remaining elements, diagonal terms are one, whereas the off-diagonal terms acquire the magnitude of zero.

For five state sub-Hilbert space, the order of multiplication is taken as

$$\mathbf{A} = \mathbf{A}_{12}(\theta_{12}) \cdot \mathbf{A}_{13}(\theta_{13}) \cdot \mathbf{A}_{14}(\theta_{14}) \cdot \mathbf{A}_{15}(\theta_{15}) \cdot \mathbf{A}_{23}(\theta_{23})$$

$$\cdot \mathbf{A}_{24}(\theta_{24}) \cdot \mathbf{A}_{25}(\theta_{25}) \cdot \mathbf{A}_{34}(\theta_{34}) \cdot \mathbf{A}_{35}(\theta_{35}) \cdot \mathbf{A}_{45}(\theta_{45})$$  \hspace{1cm} (12)$$

When this model rotation matrix and NACM are incorporated in eq 11, a set of differential equations (ADT equations) can be formulated by solving the matrix form of ADT condition. Because of the absence of any analytic solution of these differential equations, they must be integrated numerically to obtain the ADT angles which are used to construct the ADT matrix at each and every grid points in the interested domain of the nuclear CS. During the transformation of adiabatic PESs to the diabatic one, a similarity transformation [eq 10] is carried out such that the NACTs take the form of diabatic coupling elements which appear in diagonal and off-diagonal elements of the diabatic potential energy matrix.

ADT equation for “1–2” coupling of five coupled electronic states can be formulated as

$$\mathbf{V} \cdot \theta_{12} = -\bar{r}_{12} - \sin \theta_{12} \bar{r}_{13} \tan \theta_{13} + \bar{r}_{14} \sec \theta_{14} \tan \theta_{14} + \bar{r}_{15} \sec \theta_{14} \tan \theta_{14}$$

$$+ \cos \theta_{12} (\bar{r}_{23} \tan \theta_{13} \sec \theta_{13}) + \sec \theta_{14} (\bar{r}_{24} \tan \theta_{14} + \bar{r}_{25} \sec \theta_{14} \tan \theta_{14})$$  \hspace{1cm} (13)$$

If the adiabatic PESs are used for the simulation of the photoelectron spectrum of any molecule, the nonadiabatic interactions are overlooked and the inconsistency between the theoretically predicted and experimentally probed spectrum is maximum at the points of JT as well as accidental CIs. Diabatization not only removes the singularity of the NACTs but also can be used for carrying out nuclear dynamics to reproduce the photodetachment spectra and to study the reactive scattering dynamics to obtain integral cross sections.

3. DRESSED ADIABATIC, DRESSED DIABATIC, AND ADIABATIC-VIA-DRESSED DIABATIC PESs: TOPOLOGICAL EFFECTS

In a polyatomic molecule, nonadiabatic couplings could exhibit multidimensional functional behavior over the nuclear CS due to the interactions of multiple electronic states through several vibrational degrees of freedom. In order to understand the contribution of each vibrational mode on the overall nonadiabatic interactions in a molecule, detailed investigation of topological effects is the most suitable approach. Moreover, it is readily realizable that functional features of PESs and NACTs defined over a multidimensional vector space cannot be displayed in the Euclidean space because of restriction in the number of independent axes.

In our present ab initio calculation, PESs and NACTs are evaluated as functions of two normal modes ($Q_1$ and $Q_2$), keeping the other ones at their equilibrium. As a consequence, while constructing dressed potential curves (adiabatic as well as diabatic) and dressed diabatic couplings along a specific coordinate, the average effect of other mode can be embedded by integrating adiabatic and diabatic potential matrix elements over the second one. In this topological investigation, we have employed ab initio-based calculation to evaluate adiabatic PESs and NACTs and use first-principles-based transformation equations to construct diabatic PESs as a function of different pairs of normal modes, where the other modes are at equilibrium for each case. Such adiabatic and diabatic PESs are averaged over ground vibrational eigenfunctions of respective electronic states for a specific mode, and PECs are obtained to realize the topological effect originating from the other mode. The dimensionless mass-weighted normal mode coordinates can be defined as
where \( \omega_i \) and \( m_k \) signify the vibrational frequency of \( i \)th vibrational mode and atomic masses, respectively. On the other hand, \( x_{ki} \) and \( x_k^0 \) represent Cartesian coordinates at distorted and equilibrium nuclear geometry.

The dressed adiabatic potentials \( (u^Q_{\omega_i}(Q_j)) \) for \( i \)th mode and \( p \)th electronic state can be defined as

\[
u^Q_{\omega_i}(Q_j) = \langle \varphi_{p,v=0}^\ast(Q_j) | \varphi_{p,v=0}^\ast(Q_j) \rangle u_{p,v=0}(Q_j/Q_i)\]

where \( u_{p}(Q_j/Q_i)\)s represent five adiabatic PESs and \( \varphi_{p,v=0}^\ast(Q_j/Q_i) \) signifies ground vibrational eigenfunction \((v = 0)\) of the corresponding adiabatic PESs \((p)\). Here, \( u^Q_{\omega_i}(Q_j)\)s are the dressed adiabatic PESs along \( Q \) where the other effects of other normal mode \((Q)\) are averaged out.

Similarly, dressed diabatic potentials \( (W^Q_{\omega_i}(Q_j)) \) for \( i \)th normal mode and \( m,n \) electronic state can be expressed as

\[
u^Q_{\omega_i}(Q_j) = \langle \varphi_{m,v=0}^\ast(Q_j/Q_i) | \varphi_{m,v=0}^\ast(Q_j/Q_i) \rangle W_{m,n}(Q_j/Q_i)\]

When this dressed diabatic energy matrix is diagonalized, adiabatic-via-dressed diabatic potential \( (u^Q_{\omega_i}(Q_j)) \) is obtained.

Dressed adiabatic, diabatic PECs, and dressed diabatic couplings depict 1D functional form of potentials as well as couplings, where the effect of another mode is averaged out with respect to ground vibrational wavefunctions of different electronic states. It is needless to say that dressed PECs and diabatic couplings have nothing to do while studying photoelectron spectrum or performing reactive scattering calculation, but those functions can predict a lot of interesting facts about the structural features of the molecule and analytic expressions of diabatic couplings as a function of a specific coordinate. Indeed, such curves are highly useful to speculate nonadiabatic effects arising from a specific mode on the photoelectron spectrum or reactive cross sections of a molecular process. It is noteworthy to mention that not only the normal mode coordinates but also their associated polar

![Graph of potential energy curves](image_url)

**Figure 1.** Dressed adiabatic \( (u^Q_{\omega_i}(Q_j)) \), diabatic \( (W^Q_{\omega_i}(Q_j)) \), and adiabatic-via-dressed diabatic \( (u^Q_{\omega_i}(Q_j)) \) PECs \((n = 1−5)\) are depicted for (a) ground, (b) first excited, (c) second excited, (d) third excited, and (e) fourth excited states of NO3 radical along Qx. All of the PECs exhibit symmetric variation and nonlinear functional characteristics.
counterparts ($\rho$ and $\phi$) may be employed to construct dressed PECs. We can definitely perform topological study along these polar coordinates to explore their contribution on nonadiabatic interactions, but the origination of JT couplings (either sole contribution of even order polynomials, or incorporation of both linear and higher order interactions) cannot be illustrated because of the absence of any symmetric/asymmetric variations of PECs along the $\rho$ coordinate. Dressed adiabatic PECs cannot incorporate any effects of nonadiabatic coupling, whereas dressed diabatic potentials and diabatic coupling elements encompass diagonal and off-diagonal electron–nuclear couplings, respectively. While diagonalizing dressed diabatic matrix, effects of off-diagonal couplings are plugged into the newly generated adiabatic-via-dressed diabatic potentials which include both diagonal and off-diagonal nonadiabatic interactions.

4. RESULTS AND DISCUSSION

4.1. NO$_3$ Radical. In the realm of nonadiabatic chemistry, NO$_3$ radical appears to be an excellent representative system for five coupled electronic states. Several research groups have carried out thorough investigations to dig out exact equilibrium structure and complex features of photoelectron spectra. In order to achieve more structural insight, dressed potentials can be constructed by averaging out one of the normal mode coordinates. Low-lying five electronic states, namely, $\tilde{X}^2\text{A}'$ ($1^3\text{B}_2$), $\tilde{A}^2\text{E}'(1^3\text{A}_2$ and $1^3\text{B}_2$), and $\tilde{B}^2\text{E}' (1^2\text{A}_1$ and $2^2\text{B}_2$), are mainly responsible for the inherent nonadiabatic interactions. Therefore, we employ polar analogue ($\rho$ and $\phi$) of two degenerate components of in-plane asymmetric stretching vibrational mode ($\nu_3$) (symbolized as $Q_3$) to perform the ab initio calculations. This radical has been optimized employing UCCSD(T) (a spin unrestricted coupled cluster method with all single and double excitations and perturbative accounts of triple excitations) level of calculation, and the optimized parameters are presented in Table 1.\textsuperscript{37} Adiabatic PESs for five lowest electronic states\textsuperscript{19} have been already constructed using state-averaged complete active space self-consistent field (CASSCF) calculations employing 6-31g** basis set and (9e, 8o) configuration active space (CAS). On the other hand, analytic NACTs\textsuperscript{19} between the five low-lying electronic states have been obtained by implementing coupled-perturbed multi configuration space self-consistent field (CP-MCSCF) theory. In this nuclear plane, strong JT interactions are present within $E^\prime$ as well as $E^\prime$ states at three equivalent $C_{3v}$ points ($\rho \approx 3.0$ and $\phi = 30^\circ$, 150$^\circ$, and 270$^\circ$). Moreover, nonzero functional forms of $\tau^{14}$ and $\tau^{15}$ validate strong PJT interactions between ground state ($A^2\text{E}$) and the two sheets of $E^\prime$ state labeled as "1–4" and "1–5" couplings.

In order to exploit the inherent symmetry of the molecule ($D_{3h}$), ADT equations are solved for the chosen pair of normal

![Figure 2](image-url). Dressed adiabatic ($u_{\text{d}}^{Q_3}(Q_3)$), diabatic ($W_{\text{d}}^{Q_3}(Q_3)$), and adiabatic-via-dressed diabatic ($u_{\text{d}}^{Q_3}(Q_3)$) PECs ($n = 1–5$) are represented for (a) ground, (b) first excited, (c) second excited, (d) third excited, and (e) fourth excited electronic states of NO$_3$ along $Q_3$ normal mode taking average over $Q_3$. Here, the PECs are asymmetric and incorporate linear functionalities.
modes \( (Q_3x - Q_3y) \) along the \( \phi \) coordinate for each \( Q_\phi \) grid.\(^{19} \)

Our aim is to construct dressed adiabatic, dressed diabatic, and adiabatic-via-dressed diabatic potentials along \( Q_3x \) and \( Q_3y \) normal mode coordinates. Dressed adiabatic and dressed diabatic PECs are plotted as functions of \( Q_3x \) by taking average over the other normal mode coordinate \( (Q_3y) \), whereas adiabatic-via-dressed diabatic potentials can be generated by diagonalizing the dressed diabatic energy matrix \((WQ_3(Q_3x))\).

Figure 1 depicts symmetric variation of dressed adiabatic, dressed diabatic, and adiabatic-via-dressed diabatic potential energies along \( Q_3x \) mode. On the other hand, PECs plotted in Figure 2 exhibit asymmetric variation while scanning along the \( Q_3y \) mode. Such a different functional behavior originates if the component of the asymmetric stretching vibration does or does not produce equivalent geometry during positive and negative distortions. It can be observed that three PECs are widely separated in Figure 1a due to strong PJT couplings within ground \( A_2 \) and \( E' \) states. On the contrary, they almost coincide in Figure 1b and 1c because of weak JT interaction within \( E'' \) state. Finally, Figure 1d and 1e depict variation of third and fourth excited electronic states originated from JT and PJT interactions within the given range of \( Q_3x \) normal mode coordinates. Again, Figure 2 represents asymmetric functional features of PECs along \( Q_3y \) normal modes. It is noteworthy to mention that the \( Q_3x \) normal mode generates nonequivalent geometries at both sides of the equilibrium structure \( (Q_3y = 0) \). Moreover, dressed diabatic coupling elements are not only smooth, continuous, and single-valued but also exhibit similar functional characteristics of the diabatic potential. Figure 3 illustrates symmetric variation of dressed diabatic coupling terms \[ W_{23}^{Q_3x}(Q_3x), W_{45}^{Q_3y}(Q_3y), W_{14}^{Q_3y}(Q_3y), \text{ and } W_{15}^{Q_3y}(Q_3x) \] along \( Q_3x \) coordinate where the functional forms of the dressed diabatic coupling elements are constituted only with even power polynomials of \( Q_3x \). On the other hand, Figure 4 represents different behaviors of electron-nuclear couplings along positive and negative directions of the \( Q_3y \) normal mode. They lose their symmetric nature, and the corresponding functional form of coupling incorporates odd power terms.

4.2. Bz' Radical Cation. Detailed ab initio study has been already carried out to explore the nonadiabatic interactions prevailing within five low-lying electronic states of the Bz' radical cation. Further investigations are necessary to illustrate the origin and functional forms of dressed potentials as well as
dressed diabatic coupling elements. In order to reveal those functional features, we have constructed three types of dressed PECs (adiabatic, diabatic, and adiabatic-via-dressed diabatic) and dressed diabatic coupling terms along two components of the degenerate in-plane asymmetric stretching mode ($\nu_{16}$) ($Q_{16x}$ and $Q_{16y}$). This pairwise normal mode is selectively chosen because of its immense importance while depicting major inherent nonadiabaticities present in this radical cation. Before discussing our theoretical findings, a brief summary of the ab initio details$^{19}$ should be clearly mentioned for proper understanding of the newly constructed dressed PECs. Those first-principles-based quantum calculations for neutral species reveal the $D_{6h}$ symmetric structure at the equilibrium geometry, whereas the cationic species attains $D_{2h}$ point group due to intense JT distortion. In the case of Bz$^+$ radical cation, geometry optimization has been carried out implementing B3LYP (Becke, three-parameter, Lee–Yang–Parr) calculation and the optimized parameters are supplied in Table 2. Ab initio adiabatic PESs have been constructed in CASSCF methodology for the lowest five doublet states of Bz$^+$, viz, $X\tilde{2}E_1g$ (1$^2B_3g$ and 1$^2B_2g$), $B\tilde{2}E_2g$ (1$^2Ag$ and 1$^2B_1g$), and $C\tilde{2}A_2u$ (1$^2B_{1u}$) employing Gaussian basis set 6-31g** with an active space of 29 electrons distributed over 15 orbitals (29e, 15o). Moreover, analytic NACTs are obtained from CP-MCSCF methodology implemented in MOLPRO52 quantum chemistry software. Because $Q_{16x}$ and $Q_{16y}$ produce strong JT interactions within $E_{1g}$ and $E_{2g}$ states at the $D_{6h}$ point ($\rho = 0.0$), lower sheets get more stabilized and the corresponding NACTs ($\tau_{12}$ and $\tau_{34}$) tend to blow up (at $\rho = 0.0$), validating the presence of JT CIs.

In order to carry out diabatization of PESs, dimensionless mass-weighted normal mode coordinates are first converted into their polar counterparts ($\rho$ and $\phi$) to scan the entire adiabatic PESs and the NACTs. Our ultimate objective is to construct dressed adiabatic, dressed diabatic, and adiabatic-viadressed diabatic potentials along $Q_{16x}$ and $Q_{16y}$ normal mode coordinates. Figure 5 displays symmetric functional forms of dressed PECs for four lowest electronic states along the $Q_{16x}$ normal mode, whereas the PECs exhibit asymmetric behavior along $Q_{16y}$ normal mode. Figure 4. Dressed diabatic coupling terms of NO$_3$ radical along the $Q_{3y}$ normal mode. Here, (a) $W^{Q_3y}_{23}(Q_{3y})$, (b) $W^{Q_3y}_{45}(Q_{3y})$, (c) $W^{Q_3y}_{14}(Q_{3y})$, and (d) $W^{Q_3y}_{15}(Q_{3y})$ all are smooth and continuous but the variation is asymmetric. Along $Q_{3y}$ normal mode, JT coupling contains linear as well as nonlinear functionalities.

**Table 2. Optimized Geometry Parameters of Bz$^+$ Radical Cation with B3LYP Method and 6-31g(2d,p) Basis Set**

| parameters | optimization result (B3LYP) |
|------------|-----------------------------|
| bond length [C–C] | 1.382 Å |
| bond length [C–H] | 1.075 Å |
| bond angle [C–C–C] | 120.0° |
| bond angle [C–H–C–C] | 120.0° |
| normal mode frequency ($\nu_{16}$) | 1777 cm$^{-1}$ |
| equilibrium energy | $-230.7616$ a.u. |
Figure 5. Dressed adiabatic \( u_{Q_{16} n}^{Q_{16}}(Q_{16}) \), diabatic \( W_{Q_{16} n}^{Q_{16}}(Q_{16}) \), and adiabatic-via-dressed diabatic \( u_{Q_{16} n}^{Q_{16}}(Q_{16}) \) PECs \((n = 1 \rightarrow 4)\) are plotted for low-lying four electronic states of Bz\(^+\) radical cation in diagrams \((a \rightarrow d)\), respectively, along \( Q_{16} \) normal mode taking average over the other component, \( Q_{16y} \). All PECs undergo symmetric variation and include only the even order functional forms. 

along the \( Q_{16y} \) mode (Figure 6). Likewise NO\(_3\) radical, such type of interesting characteristic features are originated because of the formation of equivalent and nonequivalent geometries along \( Q_{16x} \) and \( Q_{16y} \) coordinates, respectively. For the Bz\(^+\) radical cation, three types of PECs (dressed adiabatic, dressed diabatic, and adiabatic-via-dressed diabatic) along \( Q_{16x} \) are largely separated from each other (Figure 5a−d) because of the strong JT couplings. On the other hand, those PECs are exactly superimposed for fifth electronic state because of their noninvolvement in any nonadiabatic interactions along the \( Q_{16x} \)−\( Q_{16y} \) pairwise mode. It is evident from Figure 5 that adiabatic-via-dressed diabatic curves obtained from diagonalization of dressed diabatic potential matrix exhibit one shallow minimum for ground and second excited electronic states (Figure 5a and 5c) and two shallow troughs for first and third excited ones (Figure 5b and 5d). On the other hand, asymmetric functional features of dressed PECs are exhibited along the \( Q_{16x} \) mode (Figure 6) which signify the incorporation of both odd and even power polynomials in the analytic formulation. Functional forms of dressed diabatic coupling elements also display similar trends along the two normal modes. Symmetric variation of the dressed diabatic coupling terms are represented in Figure 7a and 7b, validating the contribution of only even power polynomials for electron−nuclear couplings in the strong symmetry breaking JT interactions. On the other hand, asymmetric dressed diabatic couplings are depicted along \( Q_{16y} \) coordinate in Figure 8a and 8b, where the nonadiabatic interactions incorporate both odd and even power polynomials for couplings. Therefore, it can be concluded that JT interaction along this component \((Q_{16y})\) shows both linear and nonlinear dependence.

5. CONCLUSIONS

For the last few decades, several investigations have been carried out for highly complex scenario in the field of nonadiabatic dynamics of NO\(_3\) radical and Bz\(^+\) radical cation. In this perspective, an accurate investigation is necessary to explore the topological effects among the pairwise normal mode coordinates. Till now, nonadiabatic couplings have been extensively studied for two to five electronic state sub-Hilbert spaces\(^{19,21−24}\) to generate highly accurate diabatic PESs. On the contrary, topological studies have been carried out only for two and three coupled electronic states\(^{22−24}\) which is relevant for predicting the functional forms of dressed diabatic couplings. It is needless to say that in most cases, linear functions of normal mode coordinates are only responsible for JT stabilization, but we have already explored the sole contribution of even power couplings\(^{25,26}\) for JT and RT CIs in the case of NO\(_2\) molecule. It has been clearly revealed that selection rule for the electronic transition in NO\(_2\) molecule originates mainly because of even power coupling elements. In this article, dressed adiabatic, dressed diabatic, and adiabatic-
via-dressed diabatic electronic states are constructed for two real molecular systems of five electronic state sub-Hilbert space where one can explore the importance of even power coupling modes in JT interaction apart from the traditional ones involving both odd and even power interactions.

In Sections 2 and 3, the basic theoretical developments of BBO methodology as well as detailed background on the formulation of dressed PECs are presented explicitly and in the following section, importance of those PECs for NO$_3$ radical and Bz$^+$ radical cation is investigated. From the previous

Figure 6. Dressed adiabatic ($u_n^{\text{Q}_{16x16}}(Q_{16})$), diabatic ($W_n^{\text{Q}_{16x16}}(Q_{16})$), and adiabatic-via-dressed diabatic ($u_n^{\text{Q}_{16x16}}(Q_{16})$) PECs ($n = 1-4$) are portrayed for lowest four electronic states of Bz$^+$ radical cation in diagrams (a–d), respectively, along the $Q_{16}$ normal mode by averaging over $Q_{4ac}$. Here, PECs are asymmetric and incorporate both linear and nonlinear terms.

Figure 8. Dressed diabatic coupling terms are plotted with the variation of $Q_{16}$ normal mode coordinates of the Bz$^+$ radical cation. Figures (a,b) describe $W_{12}^{\text{Q}_{16x16}}(Q_{16})$ and $W_{34}^{\text{Q}_{16x16}}(Q_{16})$, respectively. Along $Q_{16}$ normal mode, JT coupling contains linear functions along with nonlinear terms.
It has been observed that NO$_3$ possesses several kinds of nonadiabatic interactions, namely, JT CI, accidental CI and PJT coupling, whereas the Bz$^+$ radical cation is deliberately chosen for its strong JT interaction. NO$_3$ exhibits JT interaction within E$^+$ as well as E$^-$ states, accidental CIs between two sheets of E$^-$ states along with substantial amount of PJT couplings between “1−4” and “1−5” states. Several groups have performed detailed study on the vibronic couplings to unfold its structural details and complex spectral features, but in this work, topological study for coupled electronic states is carried out for the first time. Calculated dressed diabatic coupling terms exhibit symmetric and asymmetric functional behaviors along Q$_{16x}$ and Q$_{16y}$ modes, respectively though both of the normal modes are responsible for JT coupling. Similar trend is also observed for Q$_{16z}$ and Q$_{16x}$ modes of Bz$^+$ radical cation. These modes are mainly responsible for JT CIs within E$^+$ and E$^−$ electronic states.

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Finally, we conclude that since this study validates our previous findings not only for lower but also for higher dimensional sub-Hilbert space, the effect of nonadiabaticity on molecular processes is a topological one.

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**Notes**
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**Figure 7.** Dressed diabatic coupling terms are plotted along Q$_{16x}$ normal mode of the Bz$^+$ radical cation. Figures (a,b) depict W$_{16}^{Q_{16x}}$(Q$_{16x}$) and W$_{34}^{Q_{16x}}$(Q$_{16x}$), respectively. Both are symmetric, indicating nonlinear “1−2” and “3−4” JT interactions.
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