

Excited Electronic States and Nonadiabatic Effects in Contemporary Chemical Dynamics

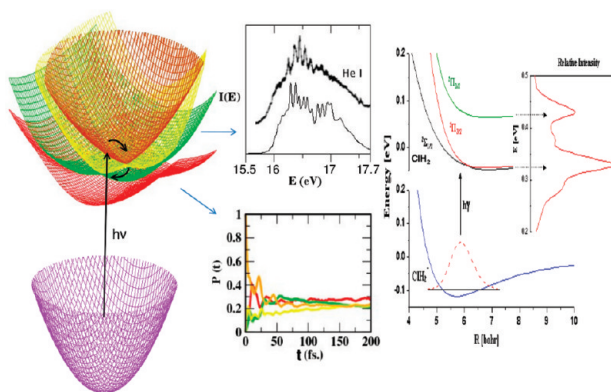
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CONSPECTUS

The question of how to describe the crossing of molecular electronic states is one of the most challenging issues in contemporary chemical dynamics. In recent years, the fundamental concept of conical intersections (CIs) of electronic potential energy surfaces (PESs) has emerged, which allows extremely fast and efficient switching of a molecule between its excited and ground electronic states. CIs are ubiquitous in polyatomic molecules. Because they generically allow the crossings of the Born–Oppenheimer (BO) adiabatic PESs, they have become the crucial mechanistic elements of the rapidly growing area of nonadiabatic chemistry. The most critical consequence of



CIs is a complete breakdown of the adiabatic BO approximation. That means that the reorganization of fast-moving electrons and nuclear vibrations must be treated concurrently. Ideally, the theoretical description should be quantum mechanical in this situation. However, because of the complexity, the necessary approximations often make it difficult to conclusively predict dynamic behavior of large polyatomic molecules. In addition, a nonunique diabatic electronic representation (describing coupling between states in the electronic Hamiltonian) is essential to avoid the singular nature of the nuclear kinetic coupling terms of the unique adiabatic electronic representation.

This Account describes both the challenges and some recent advances in quantum mechanical studies of nonadiabatic molecular processes, highlighting results from our recent work examining the static aspects of CIs and their dynamical consequences. The spectroscopic implications of the Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) intersections in complex molecular systems are discussed. Our work probes the underlying details of complex vibronic spectra of systems of growing sizes in terms of both electronic and nuclear degrees of freedom. The necessity of extension of the theoretical treatment beyond a linear vibronic coupling approach is addressed. Our results establish highly overlapping band structures due to JT and PJT CIs, a bimodal distribution of spectral intensity that originates from strong JT coupling, and the role of intermode bilinear coupling in the progressions of vibronic bands. Investigations of the quantum dynamics of the prototypical naphthalene radical cation were aimed at understanding its photostability, lack of fluorescence emissions, and diffuse interstellar bands. This work established extremely fast relaxation of this radical cation through CIs. Simulations of the interplay of electronic and relativistic spin–orbit coupling in the photodetachment spectroscopy of CH_2^- , in conjunction with experimental data, support the existence of a shallow van der Waals well in the reactive $\text{Cl} + \text{H}_2$ PES. These results also reveal a quenching of electronic coupling by the relatively strong spin–orbit coupling. In addition, we studied the dynamics of the prototypical $\text{H} + \text{H}_2$ reaction from a new perspective by explicitly including the coupling between the two energy surfaces of its JT split degenerate ground electronic state. Although individual reaction probabilities show partial sensitivity to nonadiabatic effects, the theoretical results reveal that they are not important for the dynamical outputs such as integral reaction cross sections and thermal rate constants.

I. Introduction

Contemporary advances in chemical dynamics have witnessed electronic transitions during nuclear vibrations in a wide variety of processes from spectroscopy to the dissociation of molecules. A treatment of such events necessarily is quantum mechanical (QM) extending beyond the celebrated Born–Oppenheimer (BO) approximation,¹ in which nuclear motions are decoupled from electronic motions and monitored on a single “adiabatic” electronic potential energy surface (PES). It is a challenging task, and a central quest in the new vista of chemical dynamics is to unravel the complex entanglement of electronic and nuclear motions.²

The nuclei follow non-BO or *nonadiabatic* paths when electronic states exhibit a degeneracy (or quasi-degeneracy). Two types of degeneracies are identified from a dominating linear or quadratic dependence of electronic energy on the nuclear coordinate near their vicinity.³ In the first case, electronic states cross and resemble a double cone topography, popularly known as *conical intersections* (CIs).⁴ In the second, the states do not cross but coincide and result in a glancing topography leading to Renner effect⁵ or Renner–Teller (RT) coupling. Electronic degeneracies in molecules mostly yield CIs. While point group symmetry allows a classification of different types of CIs, the RT case is unique for the degenerate electronic states of linear polyatomic molecules. Static aspects of intersections of PESs have been reviewed in the literature.^{3,6} Investigation of the nuclear dynamics through CIs is the main theme of this Account.

The premiere of CIs is a breakdown of the adiabatic or BO approximation.¹ An extension of theoretical treatments in the adiabatic electronic basis is limited by the singular nonadiabatic coupling.⁷ To circumvent it, a nonunique electronic representation called “diabatic” was invented.⁸ Furthermore, classical mechanics will not suffice because electronic transition is purely QM, particularly in the vicinity of CIs. In practice, a full quantum mechanical treatment often becomes cumbersome for systems with many electronic and nuclear degrees of freedom (DOF) and more so in the condensed phase. Methods within semiclassical and mean-field approximations have been devised for larger systems^{9,10} in which the most crucial DOF are treated quantum mechanically and the rest classically. The nonadiabatic transition is accomplished by trajectory surface hopping (TSH). These methods rely on solving the Newton equation of motion for the classical and the Schrödinger equation (SE) of motion for the quantum DOF⁹ or the Heisenberg equation that combines the features of the quantum and classical Liouville equations.¹⁰

Some of our recent works on the QM study of nonadiabatic molecular processes are reported here. These include (i) current developments in the treatment of Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) interactions¹¹ beyond a linear vibronic coupling (LVC) scheme,⁷ (ii) ultrafast nonradiative decay of electronically excited polycyclic aromatic hydrocarbon (PAH) radical cations in striving to understand their photostability and diffuse interstellar bands (DIBs), (iii) photo-detachment of ClH_2^- to probe the shallow van der Waals (VDW) well in the reactive $\text{Cl} + \text{H}_2$ PESs and to examine the novel interplay of spin–orbit (SO) and electronic coupling effects, and (iv) the electronic nonadiabatic effects on the prototypical $\text{H} + \text{H}_2$ reaction dynamics.^{4,12}

II. Conical Intersections of Potential Energy Surfaces

While crossing of electronic states of the same symmetry is prohibited by the noncrossing rule¹³ in diatomic molecules, the same does not apply to polyatomics. In the latter, the symmetry properties of the electronic states are less important due to the availability of three or more nuclear DOF. When SO interaction is excluded, the electronic Hamiltonian operator, say, $\hat{\mathcal{H}}(\mathbf{q};\mathbf{Q})$ (with \mathbf{q} and \mathbf{Q} collectively denoting the electronic and nuclear coordinates, respectively), assumes a real form. The electronic basis in which $\hat{\mathcal{H}}(\mathbf{q};\mathbf{Q})$ is diagonal defines the adiabatic representation, and its eigenvalues describe the adiabatic potential functions. These functions change abruptly with \mathbf{Q} in the neighborhood of CIs.⁷ In a diabatic electronic representation,⁸ $\hat{\mathcal{H}}(\mathbf{q};\mathbf{Q})$, remains nondiagonal, and potential energies are smooth functions of \mathbf{Q} throughout.

To proceed, let us recall a two-state diabatic Hamiltonian,

$$\mathcal{W}^d(\mathbf{Q}) = \begin{pmatrix} H_{11}(\mathbf{Q}) & H_{12}(\mathbf{Q}) \\ H_{21}(\mathbf{Q}) & H_{22}(\mathbf{Q}) \end{pmatrix} \quad (1)$$

where H_{11} and H_{22} are the diabatic PESs and $H_{12} = H_{21}$ describes their coupling. The eigenvalues of $\mathcal{W}^d(\mathbf{Q})$ can be obtained by an orthogonal transformation, $\mathbf{S}^\dagger \mathcal{W}^d(\mathbf{Q}) \mathbf{S}$, using

$$\mathbf{S}(\mathbf{Q}) = \begin{pmatrix} \cos \theta(\mathbf{Q}) & \sin \theta(\mathbf{Q}) \\ -\sin \theta(\mathbf{Q}) & \cos \theta(\mathbf{Q}) \end{pmatrix} \quad (2)$$

This yields

$$V_{1,2}(\mathbf{Q}) = \Sigma \mp \sqrt{\Delta^2 + H_{12}^2} \quad (3)$$

a double cone topography for the two adiabatic potential functions. In eq 3, $\Sigma = (H_{11} + H_{22})/2$, $\Delta = (H_{11} - H_{22})/2$ and $\theta(\mathbf{Q})$, defines the adiabatic-to-diabatic transformation (ADT) angle:

$$\theta(\mathbf{Q}) = \frac{1}{2} \arctan[2H_{12}(\mathbf{Q}) / (H_{22}(\mathbf{Q}) - H_{11}(\mathbf{Q}))] \quad (4)$$

The degeneracy of V_1 and V_2 implies, $\Delta^2 = 0$ and $H_{12}^2 = 0$. These two conditions require that Δ and H_{12} be functions of at least two independent nuclear coordinates, which forbids crossing of diatomic molecular states unless H_{12} vanishes by symmetry.¹³ Independent coordinates are available in polyatomic molecules to satisfy these conditions, and therefore, V_1 and V_2 can cross and form CIs at the degeneracy. The locus of the degeneracy defines the seam of CIs.⁴ If \mathbf{Q}_0 represent the point of degeneracy, then, as noted above, there exist two coordinates along which this degeneracy is lifted and is restored along the remaining $N - 2$ coordinates (N being the number of nuclear DOF). If H_{11} , H_{22} , and H_{12} are expanded in a first-order Taylor series around \mathbf{Q}_0 , Δ and H_{12} define the gradient difference and nonadiabatic coupling vectors, respectively. The space spanned by these vectors defines the branching space and the remaining $N - 2$ dimensions form the intersection space¹⁴ of the two PESs. When SO coupling is considered, H_{12} becomes a complex quantity, and in this case, the dimension of the seam becomes $N - 3$ if C_s symmetry is present and $N - 5$ when the number of electrons is odd.¹⁵

For illustrations, CIs of the 2B_1 and 2A_2 electronic states of phenyl radical (Ph^*) are shown in Figure 1. The perspective diagram is drawn along the coordinates of $Q_7(a_1)$ and $Q_{16}(b_2)$ representing the intersection and branching space coordinates, respectively. The PESs remain degenerate along Q_7 at the C_{2v} equilibrium configuration, and they branch out with different gradients along Q_{16} . Ph^* has ten totally symmetric a_1 vibrations along which the two PESs intersect. The seam of CIs along two of them, for example, Q_1 and Q_7 is shown in the bottom of Figure 1. The energetic minimum on this seam occurs at ~ 3.4 eV.¹⁶

It therefore emerges that CI is not an isolated point in space, but rather the PESs remain degenerate along a multi-dimensional seam. The “crucial” quantity that describes the nonadiabatic effects due to CIs is the derivative coupling of the nonadiabatic operator. In an adiabatic representation, the elements of the latter are given by⁷

$$\Lambda_{nm}(\mathbf{Q}) = -\sum_i \frac{\hbar^2}{M_i} A_{nm}^{(i)}(\mathbf{Q}) \frac{\partial}{\partial Q_i} - \sum_i \frac{\hbar^2}{2M_i} B_{nm}^{(i)}(\mathbf{Q}) \quad (5)$$

where M_i are nuclear masses and

$$A_{nm}^{(i)}(\mathbf{Q}) = \langle \Psi_n(\mathbf{q}) | \nabla_i | \Psi_m(\mathbf{q}) \rangle \quad (6)$$

and

$$B_{nm}^{(i)}(\mathbf{Q}) = \langle \Psi_n(\mathbf{q}) | \nabla_i^2 | \Psi_m(\mathbf{q}) \rangle \quad (7)$$

are the derivative coupling vector and scalar coupling, respectively. The former is nonlocal and using the Hellmann–Feynman theorem, $A_{nm}^{(i)}(\mathbf{Q})$, can be expressed as⁷

$$A_{nm}^{(i)}(\mathbf{Q}) = \frac{\langle \Psi_n(\mathbf{q}) | \nabla_i \mathcal{H}(\mathbf{q}, \mathbf{Q}) | \Psi_m(\mathbf{q}) \rangle}{V_n(\mathbf{Q}) - V_m(\mathbf{Q})} \quad (8)$$

The bra-ket notations above imply integration over \mathbf{q} only. At the CIs, $V_n(\mathbf{Q}) = V_m(\mathbf{Q})$, and $A_{nm}^{(i)}$ exhibits a singularity limiting the applicability of the adiabatic basis. This is circumvented in a diabatic representation, which relies on the removal of $A_{nm}^{(i)}$.⁸ Mathematical construction of diabatic states entails the solution of a differential equation for the ADT matrix.^{8,17} An exact solution is obtained only when the *curl* of the derivative matrix vanishes, which is difficult to achieve with a finite subset of adiabatic electronic states. Therefore, as advocated in ref 18, rigorous diabatic electronic states do not exist! In a diabatic basis, the coupling matrix reads

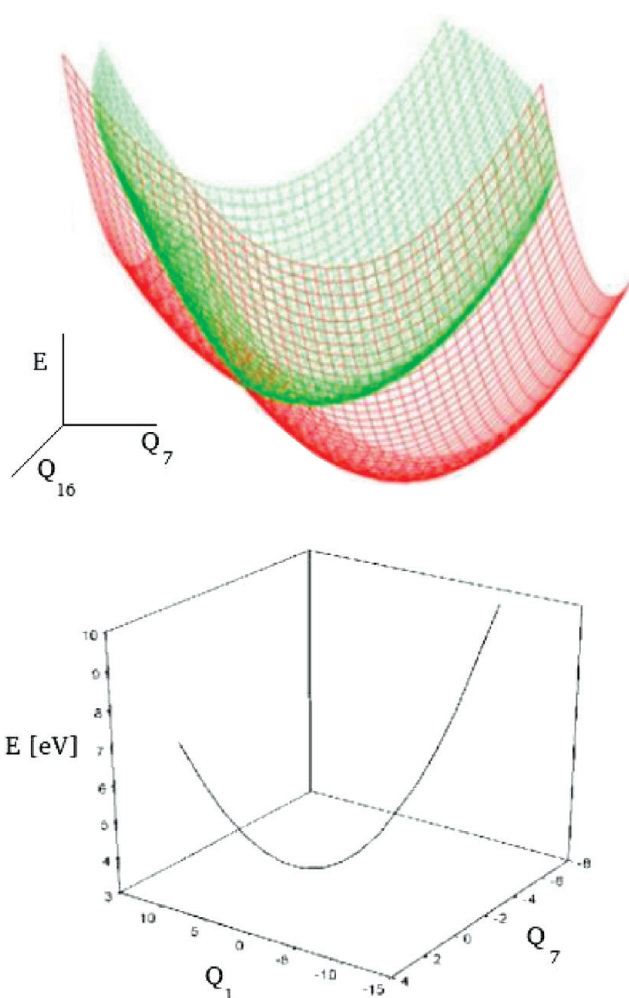


FIGURE 1. The 2B_1 – 2A_2 conical intersections of phenyl radical.

$$\mathbf{H}_{nm}(\mathbf{Q}) = \int d\mathbf{q} \psi_n^*(\mathbf{q}; \mathbf{Q}) [T_e + V(\mathbf{q}; \mathbf{Q})] \psi_m(\mathbf{q}; \mathbf{Q}) \quad (9)$$

The adiabatic electronic wave function exhibits the unique property of changing sign on encircling a close loop around CIs.⁴ This topological outgrowth, referred to as the geometric phase (GP) effect, provides an unambiguous signature of CIs.^{4c} Both the adiabatic electronic wave function and energy depend on the square root of eq 3. The analytic form of its argument vanishes, and both the wave function and the derivative of energy become discontinuous at CIs.⁴

Molecular point group symmetry generally plays a decisive role for the existence of CIs. Symmetry-enforced electronic degeneracy is exhibited by the JT systems. For example, a doubly degenerate E' state in D_{3h} symmetry configuration splits into A_1 and B_2 when distorted to C_{2v} and forms CIs at the original undistorted D_{3h} configuration. Symmetry-allowed (and accidental) CIs are ubiquitous in molecular systems.² The ${}^2B_1-{}^2A_2$ CIs of Ph^* (cf., Figure 1) provide such an example.¹⁶

III. Nuclear Dynamics through Conical Intersections

Despite an overwhelming success of TSH,^{9,10} a full QM description is certainly more desirable to simulate nuclear motions through CIs.^{2,19} A diabatic basis is resorted to avoid the stated difficulties of the adiabatic basis in the numerical simulations; however, the initial state preparation and final analysis are more realistic in the adiabatic basis. The vibronic coupling model of ref 7 is remarkably successful in treating low-amplitude nuclear motions in polyatomic molecules. This pioneering model is based on a diabatic ansatz and a Taylor expansion of the electronic Hamiltonian in terms of normal coordinates, \mathbf{Q} , of nuclear vibrations. The Hamiltonian reads⁷

$$\mathcal{H} = \mathcal{H}_0 1_n + \Delta\mathcal{H} \quad (10)$$

Here, \mathcal{H}_0 [$(n \times n)$ diagonal matrix] describes the unperturbed (harmonic) initial state, and $\Delta\mathcal{H}$ [$(n \times n)$ nondiagonal matrix] denotes the change in electronic energy upon transition to the final state, n . The elements of $\Delta\mathcal{H}$ are expanded in a Taylor series around a reference geometry in accordance with the symmetry rule $\Gamma_m \times \Gamma_{Q_i} \times \Gamma_n \supset \Gamma_A$ [Γ_m , Γ_n , and Γ_{Q_i} represent the irreducible representations (IREPs) of the electronic states m and n and the i th vibrational mode, respectively, and Γ_A is the totally symmetric representation]. A truncation of the series at the first-order term yields the LVC scheme.⁷

The eigenvalue spectrum is calculated by numerically solving the SE either by a matrix diagonalization⁷ or by a time-dependent wave packet (WP) method. The diagonalization method becomes computationally intensive for systems with large DOF, and the WP propagation within the multiconfiguration time-dependent Hartree (MCTDH) scheme significantly overcomes this problem through its multiset ansatz. For the details of the MCTDH method, the readers are referred to an authoritative review in ref 22.

Thermal reactive scattering through CIs is an emerging topic of immense current interest.² Recently the reaction cross sections and rate constants have been calculated for the $\text{H} + \text{H}_2$ reaction using flux operators and a time-dependent WP approach.^{2,23,24} The flux operator is diagonal in a diabatic basis, whereas it is nondiagonal in the adiabatic basis on par with the structure of the nuclear kinetic energy operators in the two. The expectation value of the flux operator in the basis of the scattered wave function defines the reaction probability. The reaction cross sections and the rate constants are finally derived from the reaction probabilities.

IV. The Jahn–Teller and Pseudo-Jahn–Teller Interactions

The JT effect²⁰ is a unique vibronic coupling mechanism that prevails in complex electronic spectra of symmetric molecules. Perhaps, the first evidence of CIs⁴ and the development of vibronic coupling theory thereafter stemmed from the JT systems.^{11,25} The PJT effect is attributed to a coupling of a JT state with a nondegenerate or another JT state.¹¹ The intersection of states in this case is symmetry-allowed or accidental but not enforced. In the following, we discuss the implication of JT and PJT interactions in molecular spectroscopy without being exhaustive on the vast amount of literature available on this topic.

The ($E \otimes e$)-JT effect, that is, perturbation of a doubly degenerate electronic state (E) by a doubly degenerate vibrational mode (e), has been extensively studied for molecules with trigonal symmetry.^{7,11,25–30} The e modes cease to be JT active in tetragonal systems. In this case, the JT perturbation of an E state is caused by the nondegenerate vibrational modes of b symmetry, known as ($E \otimes b$)-JT effect.^{7,11,19} The e modes can however be PJT active in both trigonal and tetragonal systems.

Within the vibronic coupling theory, the elements of $\Delta\mathcal{H}$ of eq 10 can be expanded as¹¹

$$\Delta\mathcal{H}_{\alpha\alpha'} = H_0\delta_{\alpha\alpha'} + \sum_i \frac{\partial V_{\alpha\alpha'}}{\partial Q_i} Q_i + \sum_{ij} \frac{\partial^2 V_{\alpha\alpha'}}{\partial Q_i \partial Q_j} Q_i Q_j + \mathcal{O}(Q^3) \quad (11)$$

where, H_0 is the electronic energy at the reference configuration and, $V_{\alpha\alpha'}$ ($\alpha, \alpha' = 1, \dots, n$), denote the elements of the potential matrix. The relative signs of the derivatives of $V_{\alpha\alpha'}$ and the degeneracy itself are fixed by symmetry in the JT case. For the ($E\otimes e$)-JT case, within the LVC scheme, $\Delta\mathcal{H}$ reads

$$\Delta\mathcal{H} = H_0 1 + \kappa \begin{pmatrix} Q_x & Q_y \\ Q_y & -Q_x \end{pmatrix} \quad (12)$$

where Q_x and Q_y are the components of the e mode. The Cls in this case resemble a circular double cone (cf. eq 3). Substituting, $Q_x = \rho \cos \phi$ and $Q_y = \rho \sin \phi$, in eq 12 and using eq 3 introduces a rotational symmetry, which leads to a "Mexican hat" topography²⁵ of V_1 containing three equivalent minima separated by three equivalent saddle points. In the ($E\otimes b$)-JT case, Q_x and Q_y are identified with coordinates of different b modes with different κ ;⁷ the rotational symmetry is therefore lost and the Cls resemble an elliptical double cone.⁷

We begin our discussion with the ($E + A$) $\otimes e$ JT–PJT effects (implying, PJT coupling of A state with a JT active E state and both coupling modes are e type) in CH_3CN^+ ²⁸ and CF_3CN^+ .²⁹ These radical cations have four a_1 and four e vibrational modes, and their \tilde{X} and \tilde{A} states belong to the 2E and 2A_1

IREPs of the C_{3v} point group, respectively. These states are vertically (from the reference equilibrium geometry of the corresponding neutral species) ~ 1.0 and ~ 0.5 eV spaced in CH_3CN^+ and CF_3CN^+ , respectively. A LVC model was inadequate, and therefore, a quadratic vibronic coupling (QVC) scheme (disregarding weak intermode bilinear coupling) with a linear PJT coupling was employed to examine the vibronic dynamics in these systems.^{28,29} The JT effect is weak in the \tilde{X} state of both CH_3CN^+ and CF_3CN^+ , and JT stabilization energies of ~ 0.03 and ~ 0.005 eV, respectively, were estimated.^{28,29} The \tilde{X} and \tilde{A} states of both these species are energetically close and undergo low-energy PJT crossings, particularly along the symmetric C–N stretching vibration as shown in Figure 2a. The curve crossings in it actually represent triple intersections owing to the inherent degeneracy of the JT active \tilde{X} state. The energetic minimum of the PJT Cls occurs ~ 0.68 and ~ 0.43 eV above the JT Cls in CH_3CN^+ and CF_3CN^+ , respectively.^{28,29} The PJT coupling is much stronger than the JT coupling in CF_3CN^+ , particularly along the low-frequency (~ 188 cm^{-1}) e vibrational mode of C–C–N bending plus H(F)–C–H(F) twisting type.^{28,29} PJT coupling strength of ~ 14.26 (as compared with JT coupling strength of $\sim 7.72 \times 10^{-2}$) is obtained along this mode.²⁹ A quartic expansion of JT coupling terms of the electronic Hamiltonian was necessary to describe the anharmonicity of the PESs of CF_3CN^+ along the e modes.²⁹

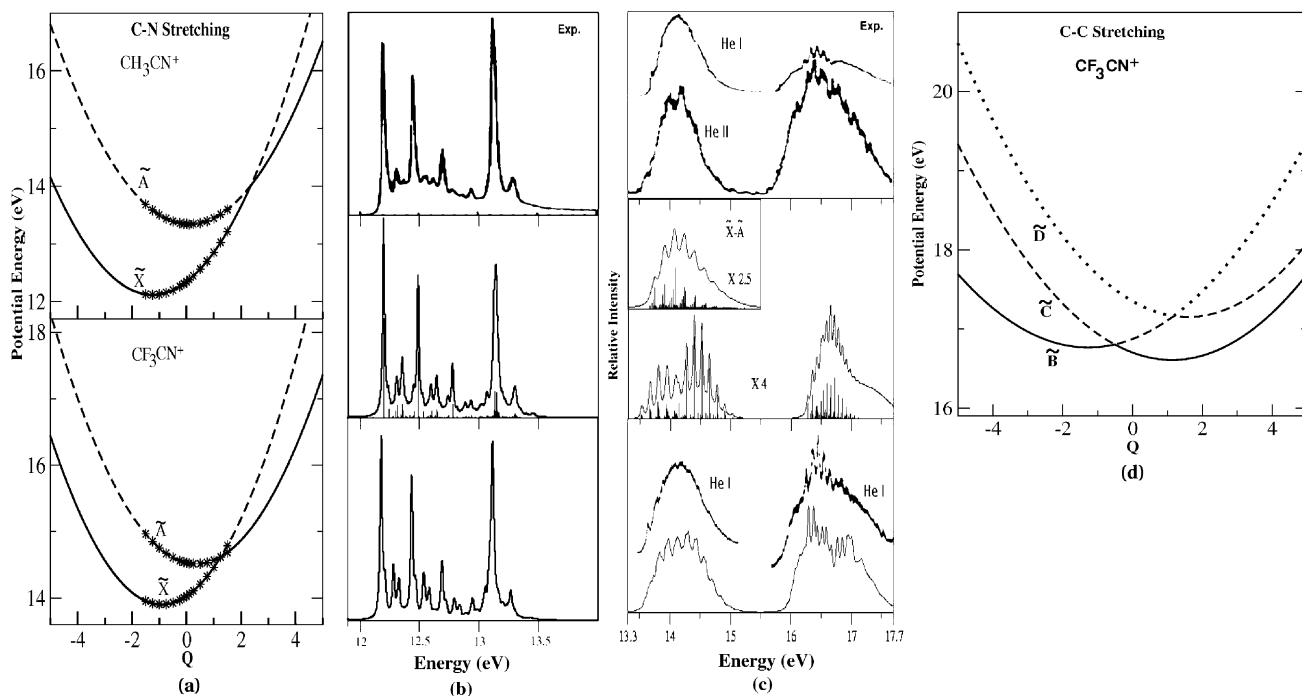


FIGURE 2. (a) Cuts of the adiabatic PESs along the symmetric C–N stretching mode obtained from the model (lines) and *ab initio* calculations (points). (b) The \tilde{X} 2E – \tilde{A} 2A_1 vibronic bands of CH_3CN^+ . (c) Same as panel b for the \tilde{X} 2E – \tilde{A} 2A_1 – \tilde{B} 2A_2 – \tilde{C} 2A_1 – \tilde{D} 2E states of CF_3CN^+ . (d) Cuts of \tilde{B} 2A_2 – \tilde{C} 2A_1 – \tilde{D} 2E states of CF_3CN^+ along the symmetric C–C stretching mode.

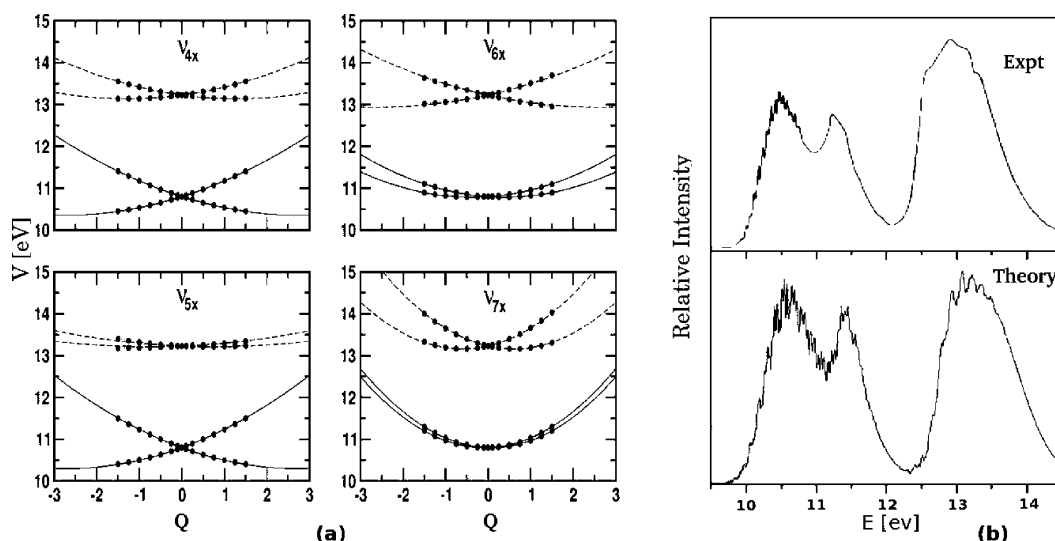


FIGURE 3. (a) Cuts of the \tilde{X}^2E' (solid line) and \tilde{A}^2E'' (dashed line) states of CP^+ along the x component of e' vibrational modes. The energies obtained from the model and calculated *ab initio* are shown by the lines and points, respectively. (b) The \tilde{X}^2E' (~ 9.5 – 12.3 eV)– \tilde{A}^2E'' (~ 12.3 – 14.5 eV) vibronic bands of CP^+ (see text for details).

While the \tilde{B} , \tilde{C} , and \tilde{D} states of CF_3CN^+ occur vertically within ~ 0.65 eV, they are widely spaced from each other and also from the \tilde{X} – \tilde{A} states in CH_3CN^+ .^{28,29} In CF_3CN^+ , these states belong to the 2A_2 , 2A_1 , and 2E IREPs, respectively, and originate from the ionization of F lone pair orbitals.

The vibronic structures of the \tilde{X} – \tilde{A} and \tilde{X} – \tilde{A} – \tilde{B} – \tilde{C} – \tilde{D} states of CH_3CN^+ and CF_3CN^+ are presented in Figure 2b,c, respectively. In each figure, the experimental, diagonalization, and WP results are shown in the top, middle, and bottom panels, respectively. The resolved structures in Figure 2b result from weak JT and PJT couplings in CH_3CN^+ ,²⁸ and the progressions therein are mostly formed by the symmetric C–N stretching, CH_3 umbrella, and degenerate symmetric/antisymmetric CH_3 vibrations. Despite some differences in the intensities, approximate diagonalization results closely resemble the converged WP results in this case.²⁸

The scenario is much more complex in CF_3CN^+ as summarized in Figure 2c. The results without and with the PJT coupling are shown in the middle and lower panels, respectively. While nearly converged \tilde{X} – \tilde{A} bands are obtained by the diagonalization method (see insert), it failed for the \tilde{B} – \tilde{C} – \tilde{D} bands (between 15.5–17.7 eV) because of huge computer overheads.²⁹ Strong mixing of levels of E and A_1 vibronic symmetries caused by the strong PJT coupling in this case leads to a huge increase of the level density and a broadening of the spectral envelope, in good accord with the experiment. The JT coupling in the \tilde{D} state is 2 orders of magnitude stronger compared with the \tilde{X} state.²⁹ Due to this and significant PJT couplings among the energetically close lying \tilde{B} – \tilde{C} – \tilde{D} states (plotted typically along the symmetric C–C stretching

mode in Figure 2d) yield the highly overlapping and diffuse bands in Figure 2c.²⁹ The symmetric C–C stretching mode is strongly excited in both the \tilde{X} – \tilde{A} and \tilde{B} – \tilde{C} – \tilde{D} bands. Peak spacings of ~ 0.144 and ~ 0.154 eV are found as compared with their (rough) experimental estimates of ~ 0.136 and ~ 0.140 eV in the two, respectively.²⁹

The JT and PJT interactions in the cyclopropane radical cation (CP^+) are more involved than discussed above. The cyclopropane (CP) molecule possesses D_{3h} symmetry in its neutral ground state, and the two lowest states of CP^+ belong to the \tilde{X}^2E' and \tilde{A}^2E'' IREPs. CP^+ has three a_1' ($\nu_1 - \nu_3$) and four e' ($\nu_4 - \nu_7$) vibrational modes. The latter are JT active in both the states. Symmetry-allowed PJT coupling between the \tilde{X} – \tilde{A} states is also possible through a_1' , a_2' and e'' vibrational modes.³⁰ Note that the JT and PJT coupling modes are different in CP^+ .

The JT effect in the \tilde{X} state of CP^+ is far stronger than that in the \tilde{A} state.³⁰ The ν_4 (CH_2 wagging) and ν_5 (ring deformation) vibrations cause an order of magnitude larger JT splitting in the \tilde{X} state. This situation is reversed for ν_6 (CH_2 scissoring) and ν_7 (asymmetric C–H stretch) vibrations as can be seen from the cuts of the PESs along the x -component of the four e' modes in Figure 3a. The JT stabilization energies of ~ 0.99 and ~ 0.64 eV were estimated for the \tilde{X} and \tilde{A} states, respectively.³⁰ The PJT coupling between them is caused by the a_1' (ν_8) and only one of the three e'' (ν_9) modes (both describe CH_2 twisting). The minimum of the seam of \tilde{X} – \tilde{A} PJT intersections occurs ~ 1.475 eV above and ~ 0.638 eV below the minimum of the JT intersections in the \tilde{X} and \tilde{A} states, respectively.³⁰

Extremely strong JT coupling of ν_4 and ν_5 modes yields a bimodal intensity pattern for the \tilde{X} band.^{30a} Because of much weaker coupling, the same is not observed for the \tilde{A} band. The vibronic bands calculated by a full QVC model including 4 states and 14 modes employing the MCTDH WP propagation approach (bottom panel) along with the experimental results (top panel) are shown in Figure 3b.^{30c} For the \tilde{X} band, the structures below ~ 11.0 eV represent progression of vibronic levels of the lower JT sheet V_1 .^{30a} Above this energy, the vibronic levels of the upper sheet V_2 show up. Strong JT coupling mixes the low-lying vibrational levels of V_2 with the quasi-continuum levels of V_1 . As a result, the bound levels of V_2 transform into metastable resonances. The second hump of the bimodal band represents such resonances of the ground vibrational level of V_2 ; known as Slonczewski resonances.³¹ Strong nonadiabatic effects due to JT interactions lead to a huge broadening of the spectral envelopes and the two maxima of the bimodal profile are ~ 0.80 eV spaced, in good accord with the experimental results of ~ 0.78 eV. Irregular progressions in the low-energy wing of the band are mainly caused by the ν_4 and ν_5 vibrational modes, and the average peak spacing of ~ 60 meV compares well with its experimental value.^{30c} It is to be noted that a LVC approach overestimates this value by ~ 40 meV,^{30a} and inclusion of the bilinear a_1-e' couplings was necessary to obtain close agreement with the experiment.^{30c}

The \tilde{A} band is highly diffuse and structureless as can be seen from Figure 3b, which is mainly caused by the strong PJT coupling due to ν_8 and ν_9 modes.³⁰ The vibronic structures of the second maximum of the \tilde{X} band and of the entire \tilde{A} band are perturbed by this coupling. The vibrational modes ν_2 , ν_3 , ν_4 , and ν_6 are predominantly excited in this band. CP^+ represents a unique example in which the PJT coupling between the two JT split states is treated for the first time.

V. Photostability of Electronically Excited Molecules

Quenching of fluorescence upon UV excitation often bears a signature of vibronic coupling and ultrafast nonradiative decay of excited electronic states. CIs "as funnels" are the bottleneck in such photochemical processes.² The dissipation of photon energy via a nonemissive path protects a molecule from more severe photoreactions and accounts for its "photostability".³² This is notably of immense importance for the aromatic amino acids and bases constituting DNA and greatly contributes to life. The mechanistic details of photostability are studied for aromatic biomolecules which reveal, for example, that their

UV photochemistry involves participation of S_0 , $^1\pi\pi^*$ and $^1\pi\sigma^*$ electronic states. The optically dark $^1\pi\sigma^*$ state connects $^1\pi\pi^*$ and S_0 electronic states via successive CIs³² and allows non-radiative transfer of the UV excited $^1\pi\pi^*$ state to the S_0 ground state.

A related quest in the current research in astrochemistry is to unravel the photostability, lack of fluorescence emission, and enigmatic DIBs of electronically excited PAH radical cations. This has instigated critical measurements of their optical spectrum in the laboratory (see, for example, ref 21 and references therein). To understand the details of the experimental observations, very recently we have performed a benchmark QM study on the prototypical naphthalene radical cation ($N^{+\cdot}$)²¹ of the PAH family. Ionization from the valence π -type MOs of the D_{2h} equilibrium ground electronic configuration of neutral naphthalene (N) yields the electronic ground $D_0(\tilde{X}^2A_u)$ and excited $D_1(\tilde{A}^2B_{3u})$ and $D_2(\tilde{B}^2B_{2g})$ states of $N^{+\cdot}$. The 48 vibrational modes of N decompose into $9a_g \oplus 3b_{1g} \oplus 8b_{1u} \oplus 4b_{2g} \oplus 8b_{2u} \oplus 8b_{3g} \oplus 4b_{3u} \oplus 4a_u$ IREPs of the D_{2h} symmetry point group. The coupling between the D_0-D_1 , D_0-D_2 and D_1-D_2 states of $N^{+\cdot}$ through b_{3g} , b_{2u} and b_{1u} modes, respectively, is symmetry-allowed, and CIs of these states have been established.²¹

To illustrate, one-dimensional cuts of the adiabatic $D_0-D_1-D_2$ PESs of $N^{+\cdot}$ are shown in Figure 4(a), along the symmetric C=C stretching a_g mode. Low-energy curve crossings seen in the figure become CIs in multidimensions. The energetic minimum of the D_0-D_1 , D_1-D_2 and D_0-D_2 CIs is found at ~ 8.47 , ~ 10.11 and ~ 13.65 eV, respectively.²¹ The D_0 , D_1 and D_1 , D_2 states are vertically ~ 0.70 and ~ 1.27 eV apart, respectively. The minimum of the D_0-D_1 CIs occurs ~ 0.1 eV above the minimum of the D_1 state and is in good accord with available data (see ref 10 of ref 21). The minimum of the D_1-D_2 CIs occurs at ~ 1.72 and ~ 0.48 eV above the minimum of the D_1 and D_2 states, respectively. The minimum of the D_0-D_2 CIs occurs at much higher energies (~ 4.0 eV above the minimum of the D_2 state) and is unimportant for the observables reported here.²¹

A critical analysis of the coupling strength of all 48 vibrational modes revealed that only 29 of them are relevant. First principles simulation of nuclear dynamics in the coupled $D_0-D_1-D_2$ states is carried out including these 29 modes employing the MCTDH WP propagation method and a QVC Hamiltonian. The resulting vibronic bands are shown in Figure 4b, along with the experimental results. The findings show that low-lying vibronic structures of the D_0 and D_2 states mostly remain unaffected by the nonadiabatic coupling and that of the D_1 state is severely affected because of energetic

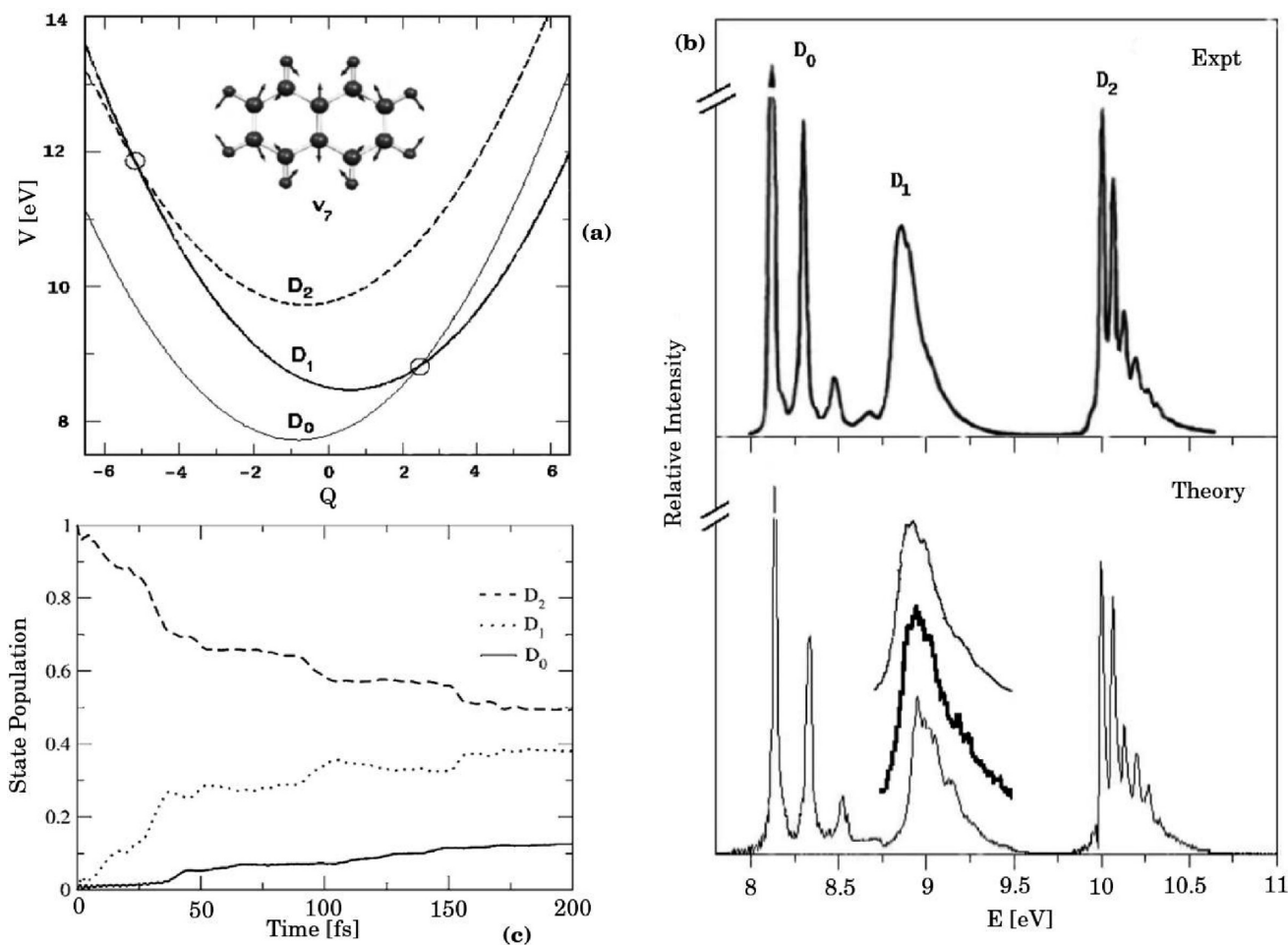


FIGURE 4. (a) Cuts of the D_0 , D_1 , and D_2 states of N^+ along the symmetric C=C stretching mode ν_7 . (b) Vibronic bands of D_0 (~ 8.0 – 8.75 eV)– D_1 (~ 8.75 – 9.5 eV)– D_2 (~ 10.0 – 10.75 eV) states. (c) Time dependence of the D_0 , D_1 , and D_2 electronic populations.

proximity of its minimum to the minimum of the D_0 – D_1 Cls. The magnified experimental D_1 band is also included in the bottom panel of Figure 4b. The overall broadening and fine structures of this band are in perfect agreement with the experiment. These findings also demonstrate that electronic nonadiabatic coupling will have a crucial role in the observed DIBs. A cavity ring down spectroscopy (CRD) experiment revealed a highly intense 0–0 peak of the optically bright D_2 state, which is in good accord with the results of Figure 4b. Progression due to the lowest frequency symmetric skeletal vibration (~ 514 cm^{-1}) dominates in this band in accord with the experiment.²¹

The time dependence of D_0 , D_1 , and D_2 diabatic electronic populations upon initial excitation to the D_2 state is shown in Figure 4c. The initial decay of the D_2 state population is estimated to occur on a time scale of ~ 217 fs, in good accord with the experimental results of ~ 212 fs²¹ and supports the observation of lack of fluorescence emission and photostability of this state. A much faster decay rate of ~ 29 fs is estimated for the D_1 state.²¹

VI. Reactive Potential Energy Surfaces and Nonadiabatic Interactions

Photodetachment spectroscopy of ClH_2^- has allowed a breakthrough in probing the shallow VDW well in the reactive $\text{Cl} + \text{H}_2$ PES for the first time.³³ Both the electronic and SO couplings are relevant for this system, and its low-lying adiabatic states are of $^2\Sigma_{1/2}$, $^2\Pi_{3/2}$, and $^2\Pi_{1/2}$ type in the collinear and $1^2A'$, $1^2A''$, and $2^2A'$ type, respectively, in the noncollinear configurations.³⁴ The $^2\Sigma_{1/2}$ SO state only correlates to the electronic ground state of products, $\text{HCl}(\tilde{X}^1\Sigma^+) + \text{H}(^2S)$. The other two states yield the ground-state products via nonadiabatic transitions to the $^2\Sigma_{1/2}$ state.

The photodetachment of ClH_2^- is depicted in Figure 5a. The adiabatic PESs of the ground electronic state of ClH_2^- ³⁵ and the three SO states of ClH_2 ³⁴ are plotted along R (Cl to the center-of-mass of H_2 distance), for $r = 1.402a_0$ (H_2 internuclear distance) and $\gamma = 0^\circ$ (angle between \vec{R} and \vec{r}). The ground vibrational wave function of ClH_2^- is also shown in the diagram. The VDW well (~ 0.5 kcal/mol) on the ClH_2 PES occurs

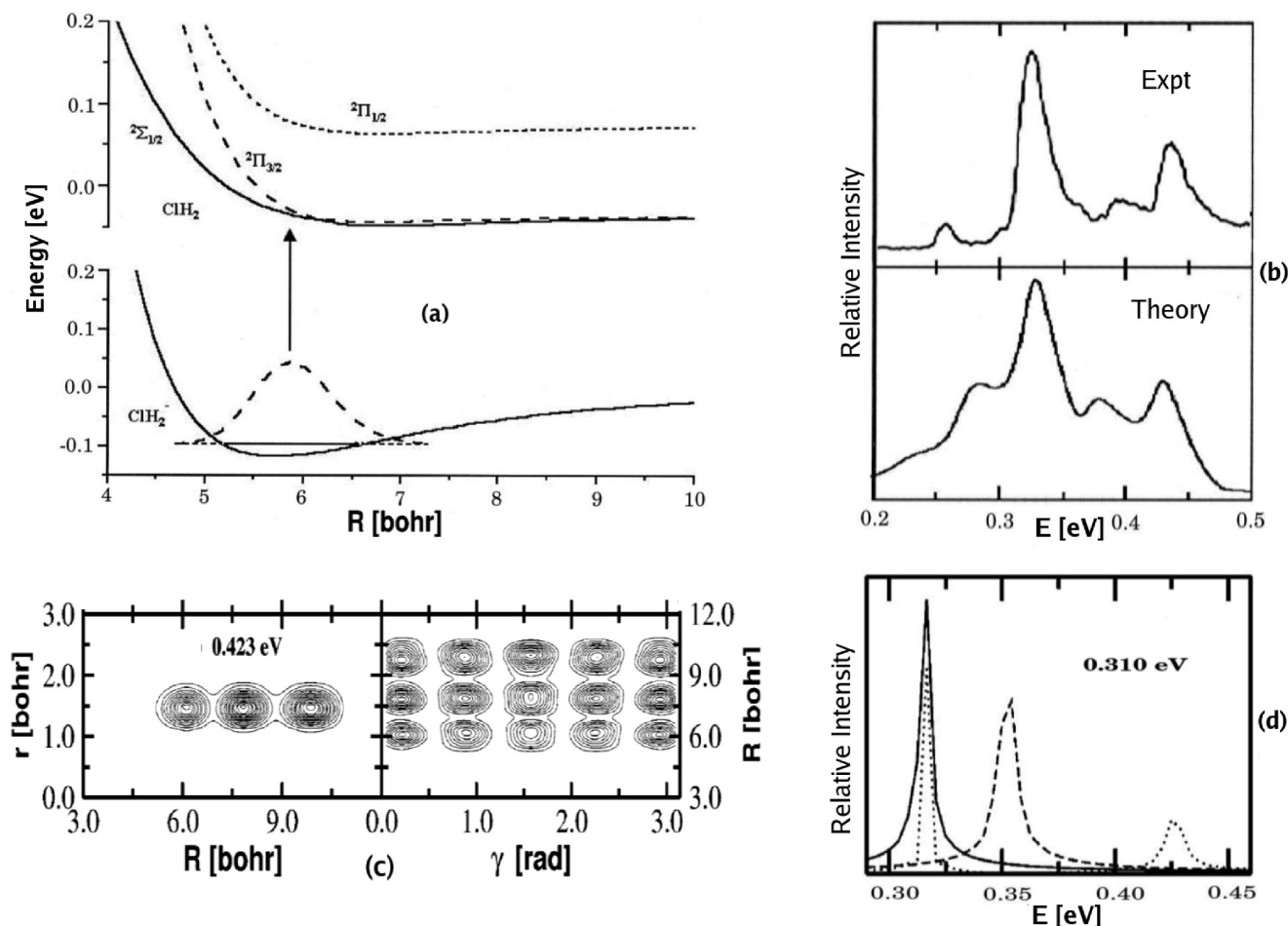


FIGURE 5. (a) Schematic drawing of the photodetachment spectroscopy of ClH_2^- . (b) Photodetachment spectrum of ClH_2^- (see text for details). (c) Progressions in the 0.423 eV resonance and (d) interplay of electronic and SO coupling on the 0.31 eV resonance of the $^2\Sigma_{1/2}$ SO state of ClH_2 .

at the T shaped geometry at $R \approx 5.78a_0$,³⁴ whereas the equilibrium minimum on the ClH_2^- PES occurs at the linear geometry at $R \approx 5.714a_0$.³⁵ Despite this difference, the anionic wave function is very diffuse along γ and exhibits a good Franck–Condon (FC) overlap with the VDW well.³⁶

The photodetachment spectrum of ClH_2^- was examined by employing the following diabatic Hamiltonian for ClH_2 ³⁶

$$\mathcal{H} = \mathcal{H}^{\text{Nu}}1_3 + \begin{pmatrix} V_\Sigma & -V_1 - i\sqrt{2}B & V_1 \\ -V_1 + i\sqrt{2}B & V_\Pi + A & V_2 \\ V_1 & V_2 & V_\Pi - A \end{pmatrix} \quad (13)$$

where \mathcal{H}^{Nu} is the nuclear Hamiltonian and A and B represent Π – Π and Σ – Π SO interactions, respectively.³⁶ Three partial spectra were calculated for initial FC transition of the anion to each of the three diabatic electronic states of the neutral and evolving the WP with the aid of time-dependent-Schrödinger equation and the Hamiltonian of eq 13. The calculations were restricted to the total angular momentum J

$= 0.5$. The autocorrelation functions were recorded in time and Fourier transformed to generate the spectrum. The results from three calculations were combined and finally convoluted with a Lorentzian function of 20 meV full width at the half-maximum (fwhm) to generate the composite photodetachment spectrum.³⁶ The results are presented in Figure 5b along with the experimental data of ref 33. The overall agreement between the two is intriguing. The individual peak structures are found to originate from highly overlapping transitions to all three SO states of ClH_2 .³⁶ The two major peaks are separated by CI SO coupling of ~ 0.102 eV, in good accord with the experimental estimate of ~ 0.111 eV.³³ The electronic coupling is found to have an insignificant role compared with the SO coupling in broadening the spectrum.³⁶ Fine structures underneath each peak reveal extended progressions of VDW resonances along R and γ as shown typically for the 0.423 eV peak in Figure 5c.³⁶ Novel interplay of electronic and SO coupling on these resonances is also established. This is exemplified typically with the 0.31 eV resonance of the $^2\Sigma_{1/2}$ PES

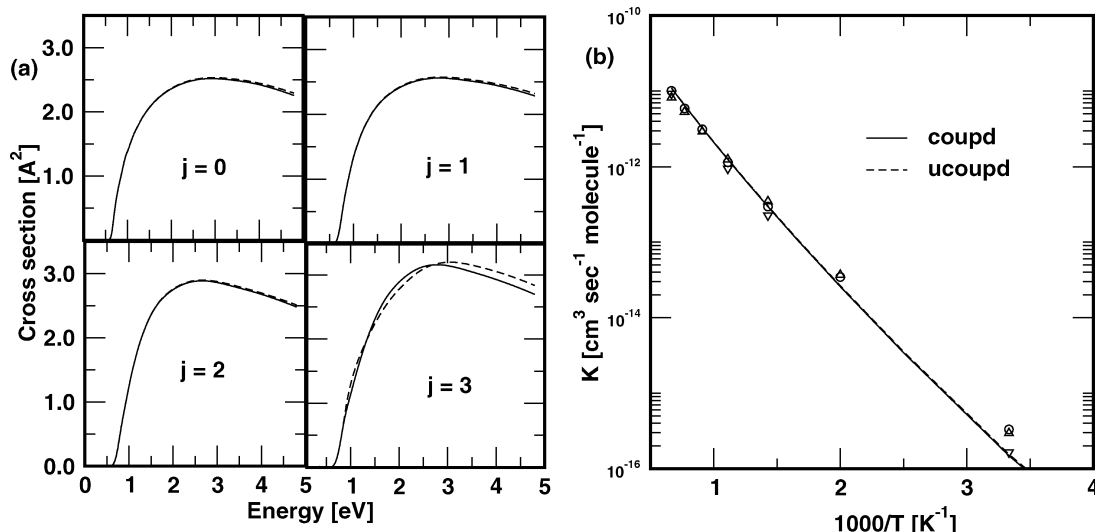


FIGURE 6. (a) ICSSs of $\text{H} + \text{H}_2 (\nu = 0, j) \rightarrow \text{H}_2(\Sigma\nu, \Sigma j) + \text{H}$. (b) Thermal rate constant of $\text{H} + \text{H}_2 (\nu = 0)$ reaction.

in Figure 5d. The sharp peak (solid line) at 0.31 eV represents the uncoupled surface results and shifts by ~ 0.035 eV to higher energy due to GP effects when electronic coupling is included (dashed line). With SO coupling in addition, the peak splits into two (dotted line), which are separated by ~ 0.11 eV, equal to the CI SO splitting.³⁶ Furthermore, the low-energy peak returns to its uncoupled state location at ~ 0.31 eV revealing a quenching of electronic coupling effects by the relatively stronger SO coupling.³⁶ This is in accordance with the discussions by Mead¹⁵ that when SO coupling is included, PES crossings tend to become avoided and the single-valuedness of the electronic wave function is retained.

The above investigations represent the first theoretical work of its kind to reveal the impact of electronic and SO coupling in the photodetachment spectrum of ClH_2^- , and the results corroborate to the experimental discovery of a shallow VDW well in the $\text{Cl} + \text{H}_2$ PES.^{33,36} We note that the theoretical results discussed above are obtained on a relatively coarse grid and for the lowest value of the total angular momentum using a diabatic representation throughout. Further refinements by relaxing these constraints are necessary in order to provide a more quantitative account of the subject.

VII. Nonadiabatic Chemical Reaction Dynamics

Electronic nonadiabatic effects in chemical reaction dynamics is an emerging topic, and attempts have been made to investigate them quantum mechanically recently.² The $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ exchange reaction has been a benchmark prototype model for understanding microscopic details of formation and breakage of chemical bonds. The electronic ground state of H_3 is orbitally degenerate (${}^2\text{E}$) and is liable to JT insta-

bility. The two JT split component states form CIs at the D_{3h} configuration. The $\text{H} + \text{H}_2$ exchange reaction occurs on the repulsive lower adiabatic component (V_1). A major interest in the current literature is to unveil the role of the bound upper adiabatic component (V_2) on the dynamics of this reaction.^{2,23,24} In this spirit, the latter is simulated on V_1 including the GP change to account for the nonadiabatic effects.³⁷ The results established only minor GP effects on the reaction cross sections for energies beyond 1.8 eV.³⁷ The small GP effects observed in the reaction probabilities for various values of J average out in the reaction cross sections.

Since the GP change represents only a part of the nonadiabatic coupling effects, the $\text{H} + \text{H}_2$ reaction dynamics is also studied by including explicit coupling between V_1 and V_2 and propagating WPs employing the diabatic Hamiltonian^{2,23,24}

$$\mathcal{H} = \left(T_N + \frac{V_1 + V_2}{2} \right) 1 + \frac{V_2 - V_1}{2} \begin{pmatrix} -\cos\alpha & \sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} \quad (14)$$

Here T_N is the nuclear kinetic energy operator, and $\alpha = 2\theta$ represents the pseudorotation angle (see, ref 39 for details). The adiabatic PESs of ref 38 are used for V_1 and V_2 .

Integral reaction cross sections (ICSSs) up to a three-body dissociation energy of ~ 4.74 eV were calculated from reaction probabilities obtained using the flux operators discussed above. The initial WP was prepared on the reagent asymptote of V_1 and then propagated with the aid of the above Hamiltonian expressed in reagent Jacobi coordinates (R, r, γ) (see section IV).²⁴ Partial wave contribution for J up to 50 was necessary to obtain the converged ICSSs. The results for $\text{H} + \text{H}_2 (\nu = 0, j)$ are shown in Figure 6a for different values of H_2 rotational quantum number j . The uncoupled and coupled surface results are shown by the dashed and solid lines,

respectively. Minor differences between the two results are seen only when H_2 is excited to $j = 3$. The Boltzmann averaged (over $j = 0-3$) thermal rate constants for $H + H_2$ ($\nu = 0$) reaction shown in Figure 6b also reveal insignificant effects of the surface coupling on the dynamics. Minor differences between the coupled and uncoupled surface results beyond ~ 2.74 eV (the minimum of the seam of JT CIs of V_1 and V_2) and their good agreement with the GP and experimental results brought the "saga" to an end, to conclude that the important dynamical observables like ICs and rate constants derived from the reaction probabilities are insensitive to the nonadiabatic coupling, even though the latter show some variations over the considered energy range.²⁴ The minimum energy path for this reaction occurs for the collinear arrangements with a classical barrier height of ~ 0.42 eV.³⁸ Therefore, a major part of the reactive flux is routed via this path, apparently also for higher energies. Less than $\sim 1\%$ WP reaches V_2 during the entire course of the reaction for all values of J .²⁴

VIII. Summary

Some recent advances on the quantum mechanical treatment of gas-phase nonadiabatic chemical dynamics are presented here. The crossings of electronic states, in particular, the ubiquity and role of CIs in molecular spectroscopy, and reaction dynamics are rationalized by simulating nuclear motions through them. The JT and PJT effects for very weak to very strong coupling situations are demonstrated, attesting the necessity to go beyond the LVC approach to recover the potential anharmonicity. Ultrafast nonradiative decay of electronically excited PAH radical cations unravels the quenching of fluorescence and their photostability and contributes to the understanding of DIBs. The success of the MCTDH WP propagation approach over the diagonalization approach for multimode vibronic dynamics is revealed to describe low-resolution spectra. However, the latter should be the method of choice for high-resolution applications. The interplay of electronic and SO coupling in the photodetachment spectroscopy of ClH_2^- is revealed, corroborating the existence of a shallow VDW well in the reactive $Cl + H_2$ PES. The issue of the GP effects in the prototypical $H + H_2$ reaction is unveiled by a time-dependent WP treatment of the dynamics by explicitly including the coupling between the two sheets of its JT split ground electronic state. Further advancements are desired to treat multimode dynamics of more complex systems in complex environments. These include identification of the most relevant DOF and treatment of the nuclear dynamics on cou-

pled electronic states in a suitable coordinate system to model molecular vibrations and chemical reactions.

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BIOGRAPHICAL INFORMATION

Susanta Mahapatra received his M.Sc. (1991) in chemistry from the Banaras Hindu University and a Ph.D. (1996) in theoretical chemistry from I. I. T. Kanpur with N. Sathyamurthy. He did post-doctoral work with L. Zülicke at the University of Potsdam (1996–1997) and with H. Köppel and L. S. Cederbaum at the University of Heidelberg (1997–2000) and joined the faculty of the School of Chemistry, University of Hyderabad, in October 2000 where he is currently a professor. His research mainly focuses on the quantum mechanical studies of nonadiabatic chemical dynamics.

FOOTNOTES

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