A quantum-classical simulation of the nuclear dynamics in NO_2^- and C_6H_6^+ with realistic model Hamiltonian

SUBHANKAR SARDAR, AMIT KUMAR PAUL and SATRAJIT ADHIKARI*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032

e-mail: pcsa@iacs.res.in

MS received 13 August 2009; revised 18 May 2010; accepted 27 May 2010

Abstract. We perform the nuclear dynamics simulation to calculate the broad band as well as better resolved (a) *photodetachment* spectra of nitrogen dioxide anion (NO_2^-), and (b) *photoelectron* spectra of benzene radical cation (C_6H_6^+) with *degeneracy* among the electronic states using our *parallelized* time dependent discrete variable representation approach. For this purpose, we first consider a theoretical model that describes the photodetachment spectrum originating due to the Franck–Condon (FC) transition from the anionic ground state to the conically intersecting $\tilde{X}^2A_1 - \tilde{A}^2B_2$ electronic manifold of the neutral NO_2 , whereas two multi-state, multi-mode model Hamiltonians of C_6H_6^+ with degeneracy among the electronic states are explored for its photoelectron spectra. The dynamics of C_6H_6^+ has been carried out with two Hamiltonians: (a) one consists with *four states and nine modes*, and (b) the other is constituted with *three states and seven modes*. Since the electronic states of both the systems are interconnected by several conical intersections in the vicinity of the FC region, it would be challenging to pursue the dynamical calculation due to the impact of non-adiabaticity among the electronic states. The spectral profiles obtained with the advent of TDDVR approach show reasonably good agreement with the results obtained by other theoretical methodologies and experimental measurements.

Keywords. Nitrogen dioxide anion; benzene; benzene radical cation; TDDVR method; quantum classical approach; conical intersection; multi-state multi-mode dynamics.

1. Introduction

Photoelectronic transitions, generally occurring from lower electronic surfaces to different upper states, lead to rapid (in femto second time scale) depopulation of the system to lower ones and produce several photoelectronic band structure of various ionized and neutral molecules. These electronic states are frequently coupled with the nuclear motion, where the strong interaction among the states customarily known as vibronic coupling (VC) gives rise to dramatic failure of familiar adiabatic or Born–Oppenheimer (BO) approximation, especially for the existence of conical intersections (CIs) within or close to the Franck–Condon (FC) region. Such phenomena demonstrate that nuclear motion has to be monitored simultaneously on all surfaces instead of only one potential energy surface (PES). The CIs significantly affect the molecular dynamics and henceforth, the population transfer which con-

struct a complex spectral appearance of the molecular system. There are several experimental investigations on such systems leading to many theoretical calculations considering non-adiabatic processes^{1–14} involved in the dynamics.

Since the non-adiabatic coupling terms among the states, particularly in the presence of CI(s) generate pure quantum mechanical (QM) features, those terms demand rigorous QM treatment¹⁵ to calculate dynamical properties. However, the solution of time-dependent Schrödinger equation (TDSE) for those systems is restricted by the computational time that increases exponentially with the number of degrees of freedom (DOFs), particularly when atoms are heavy, the energy separation is high and multiple PESs are involved. In this situation, the motivation to formulate a quantum dynamics approach to explore relatively large molecular system is a growing area of current interest. The quantum correction to classical dynamics is one of the usual way to develop first principle based quantum-classical approaches, which can distinguish both quasi-classical

*For correspondence

and deep quantum regime and thereby, treat the quantum modes rigorously and quasi-classical ones classically with some mild quantum correction. On the other hand, traditional time-dependent approaches use stationary grid points/basis set to represent a wave function and waste many grid points/basis set to specify empty space. The methods consisting time-dependent basis functions or moving grid points may have the possibility to achieve convergence significantly fast.

The formulation of molecular dynamics approach by using Gaussian Wave Packet (GWP)¹⁶ and its' extension, the Gauss-Hermite (GH) basis set,¹⁷⁻²² is physically appealing and conceptually important to meet the two major requirements for pursuing calculations on relatively large systems: (a) the distinction of quasi-classical and deep quantum regimes; (b) the movements of the basis functions with time. When the wavefunction is expanded in terms of GH basis functions and inserted in the TDSE, the time-dependent parameters of GWP appear naturally in the 'classical' equation of motion with more generalized force. Even though kinetic energy (KE) operators are local with the use of GH basis function, the major focus is the evaluation of matrix elements over the potential at each time step. A huge amount of CPU time goes for calculating those matrix elements, where the accuracy and efficiency of the time propagation for the 'classical' parameters are the bottleneck for fast convergence. Moreover, the variationally optimized 'classical' equation of motion^{20,22} for GWP parameters are usually stiff and then, increase computational time and inaccuracy²³⁻²⁵ extensively.

The time dependent discrete variable representation (TDDVR) method²⁶⁻³⁹ takes the advantages of both DVR and time-dependent basis. TDDVR is a very convenient formulation with the following attributes: (a) a very few number of optimized set of asymmetrically dense grid-points are used which are generated from the Hermite polynomial associated with the eigenfunction of a harmonic oscillator defined around the center of an initial wave packet, GWP; (b) the classical dynamics of the time-dependent parameters of GWP dictates the movement of these unevenly spaced grid-points; (c) though the evaluation of KE matrices is needed once for the entire propagation, the diagonal potential energy (PE) matrix by which the electronic states are coupled has to be calculated at each time-step; (d) the independent contributions of different modes on

a time-dependent amplitude motivate us to parallelize the algorithm which reduces the computational time remarkably.³⁷⁻³⁹ The formulation has the following assumptions on the form of the molecular wavefunction: (a) the wavefunction on each surface is being expanded as sum of vectors, namely product-type multi-mode TDDVR basis functions with time-dependent coefficients. When this multi-dimensional multi-surface wavefunction matrix is substituted in the TDSE, we find that the time-dependence of the expansion coefficients measure the quantum dynamics where the classical equation of motion for the central trajectory and its' momentum appear naturally; (b) time evolution of the amplitudes on the grid points comes through quantum dynamics and movement of the grid points is obtained from classical mechanics where grid points are associated with a distribution of 'classical' momenta; (c) the formulation has enough scope to incorporate the details associated with the respective surface through TDDVR basis set as well as time-dependent coefficients while moving from one surface to another; (d) each TDDVR basis function is originated due to multiplication of the corresponding DVR basis with a plane wave which differs from one surface to another by its' parameter; (e) the eigenfunctions of harmonic oscillator constructs the DVR basis set; (f) the plane wave is defined by a classical trajectory and its' momentum. In this regard, it is worthy to mention that the formulation is based on time-independent width parameter²⁸⁻³⁴ to bypass the inaccuracy²⁶ in the quantum equation of motion as well as the stiffness in the classical equation of motion due to time-dependent width parameter. When enough trajectories are included, the method is numerically exact, whereas with one grid point, one can recover the classical molecular dynamics approach. It is precious to note that TDDVR with one grid-point corresponds to the classical limit known from Newtonian force. In our previous articles,^{32,33,35} different computational aspects of TDDVR method and other contemporary time-dependent techniques, viz. nested interaction representation method,^{40,41} distributed approximating function approach⁴² and other time-dependent DVR method⁴³ are described elaborately in a comparative manner.

The ultraviolet photoelectron (PE) spectrum of NO₂ is obtained experimentally with the aid of negative ion photoelectron spectroscopy⁴⁴ by measuring the KE of photodetached electrons from the follow-

ing reaction: $\text{NO}_2^-(\nu'') + h\nu = \text{NO}_2(\nu') + e^-$, where ν'' and ν' denote the vibrational states of the ionic and neutral species, respectively. The PE spectrum of NO_2^- is not only difficult for experimentalists^{45,46} but also its' spectral simulation is a great challenge for theoreticians^{47–51} because a series of CIs are prevailed among the three low-lying electronic excited states, viz. $\tilde{A}^2\text{B}_2$, $\tilde{B}^2\text{B}_1$, $\tilde{C}^2\text{A}_2$ and the ground state, $\tilde{X}^2\text{A}_1$. The first explanation of the $\tilde{X}^2\text{A}_1 - \tilde{A}^2\text{B}_2$ band of NO_2 was given by Haller *et al.*⁴⁷ and much later, Leitner *et al.*⁴⁹ explored the correspondence between spectral statistics and classical dynamics of the molecule. Mahapatra *et al.*⁵⁰ used a model Hamiltonian within the so called linear vibronic coupling (LVC) scheme⁶ with the help of *ab initio* data obtained by the Hirsch *et al.*⁵² and successfully represented the low resolution spectra (266 nm) of Weaver *et al.*⁴⁵ and the high resolution (351 nm) spectrum⁴⁶ with higher order correction in their LVC model. In this article, we perform dynamics with the help of TDDVR methodology by using the model Hamiltonian developed by Mahapatra *et al.*⁵⁰

The first explanation of the diffuse appearance of $\tilde{B}^2\text{E}_{2g} - \tilde{C}^2\text{A}_{2u}$ band in PE spectra of C_6H_6^+ was given by Köppel *et al.*⁵³ As an extension of earlier work, Köppel⁵⁴ pointed out the combined multi-mode Jahn–Teller (JT) splitting of the additional state $\tilde{X}^2\text{E}_{1g}$ with the $\tilde{B}^2\text{E}_{2g}$ and $\tilde{C}^2\text{A}_{2u}$ PESs. Further theoretical studies on this system lead to satisfactory agreement of diffuse appearance of the *ab initio* calculated envelop⁵⁵ with experimental $\tilde{D}^2\text{E}_{1u} - \tilde{E}^2\text{B}_{2u}$ band of the PE spectra. In all these theoretical studies,^{53–59} the spacial degeneracy of the states ($\tilde{X}^2\text{E}_{1g}$, $\tilde{B}^2\text{E}_{2g}$, $\tilde{D}^2\text{E}_{1u}$) at low energy was considered to demonstrate such highly complex dynamics of this typical organic cation. As we have already carried out the dynamics of benzene radical cation including five nondegenerate surfaces,^{37,39} it will be interesting to explore the nuclear dynamics of the same molecule, where the Hamiltonian is constituted either with one or two doubly degenerate electronic states.⁵⁹

The present paper is organized as follows: In the following section 2 we briefly discuss about the Hamiltonians adopted for dynamical calculation. We introduce the theoretical background of our TDDVR method in section 3. Next two sections, 4 and 5, are devoted for initialization, projection of the wave function and spectral analysis. The section 6 describes the numerical details of our time-dependent

dynamical calculations. The section 7 consists of the most elaborate part of our study where the results of our present theoretical investigations have been discussed. The advantages of parallelized TDDVR code over serial one are demonstrated in the next section 8. We summarize the different perspectives of our TDDVR method in the final section 9.

2. The realistic model Hamiltonian

2.1 NO_2^- system

The purpose of our first dynamical calculation is *not only* to explore the workability of *parallelized* TDDVR approach on a realistic two-surface ($\tilde{X}^2\text{A}_1$ and $\tilde{A}^2\text{B}_2$) three mode model Hamiltonian to reproduce the experimental^{45,46} and theoretically calculated⁵⁰ photodetachment spectra of NO_2 , *but also* to provide a classical interpretation of the time-dependent dynamics using a quantum-classical methodology. Since the two electronic states interact via a VC mechanism, the beyond BO effects are introduced through linear and higher order coupling terms. In the adiabatic representation, the couplings among the states appear in the KE operator and coupling elements could be singular at and around the point or along the seam of CI(s) and therefore, the use of diabatic Hamiltonian is essential. The detailed description of the system dynamics requires a suitable model Hamiltonian that incorporates the symmetry properties of the molecule expecting to reproduce the PE spectra of the NO_2^- and to provide the explanation of the ultrafast relaxation processes. The explicit form of the Hamiltonian introduced by Mahapatra *et al.*⁵⁰ for low resolution spectra considers the aforesaid aspects of the system as given below:

$$\hat{H} = (\hat{T}_N + \hat{V}_0)\mathbf{1} + \begin{pmatrix} \mathbf{a} & \mathbf{c} \\ \mathbf{c} & \mathbf{b} \end{pmatrix}, \quad (1)$$

where

$$\hat{T}_N = -\frac{1}{2} \sum_{i=1}^2 \omega_i \left(\frac{\partial^2}{\partial Q_i^2} \right) - \frac{1}{2} \omega_3 \left(\frac{\partial^2}{\partial Q_3^2} \right), \quad (2a)$$

$$\hat{V}_0 = \frac{1}{2} \sum_{i=1}^2 \omega_i Q_i^2 + \frac{1}{2} \omega_3 Q_3^2, \quad (2b)$$

and

$$a = E_X^0 + \sum_{i=1}^2 \alpha_i^{(1)} Q_i, \quad (2c)$$

$$b = E_A^0 + \sum_{i=1}^2 \alpha_i^{(2)} Q_i, \quad (2d)$$

$$c = \lambda Q_3. \quad (2e)$$

The two terms $\hat{T}_N$ and $\hat{V}_0$ denote the KE and PE term for the unperturbed harmonic oscillators of all the vibrationally active modes in the system, respectively, whereas the 2×2 unit matrix is represented by **1**. The quantities E_k ($k = \tilde{X}, \tilde{A}$) indicates the vertical ionization potential (IP) of the corresponding electronic states as presented in table 1 with the frequency values and coupling constants. In the above mentioned Hamiltonian (1), the totally symmetric modes (ν_1, ν_2) act as tuning modes,

whereas the non-totally symmetric mode (ν_3) serves as a coupling mode. The linear intrastate (α_i , where $i = 1, 2$) and inter state (λ) coupling constant of the above mentioned Hamiltonian (1) are considered to obtain broad band spectrum. Moreover, in order to simulate better resolved (391 nm) $\tilde{X}^2 A_1$ band, the linear parameters, a and b, are expanded up to second order terms, which are denoted by a' and b' as:

$$a' = E_X^0 + \sum_{i=1}^2 \beta_i^{(1)} Q_i + \gamma_{11} Q_1^2 + \gamma_{22} Q_2^2 + \gamma_{12} Q_1 Q_2 \quad (3a)$$

$$b' = E_A^0 + \sum_{i=1}^2 \beta_i^{(2)} Q_i + \gamma_{11} Q_1^2 + \gamma_{22} Q_2^2 + \gamma_{12} Q_1 Q_2. \quad (3b)$$

It is worthwhile to mention that we consider the second order Hamiltonian with ($\lambda = 0.087$) or without ($\lambda = 0.0$) coupling between the two electronic states.

Table 1. Numerical parameters are adopted from ref 50 and used in the dynamical study of NO_2^- using the LVC Hamiltonian (1).

	ω	$\tilde{X}^2 A_1$	$\tilde{A}^2 B_2$
α_1	0.093	0.218	-0.260
α_2	0.167	0.271	-0.156
λ	0.206	0.087	
E		0.4756	1.620

Table 2. The *ab initio* calculated coupling constants, frequencies and vertical IPs used in the dynamical study of C_6H_6^+ using the LVC Hamiltonian (4). The numerical data presented below are reproduced from ref. 59.

	ω	$\tilde{X}^2 E_{1g}$	$\tilde{B}^2 E_{2g}$
ν_1	0.4081	0.0271	-0.1163
ν_2	0.1257	0.0467	0.0467
ν_{16}	0.2055	0.1643	0.3276
ν_{17}	0.1497	0.0764	
ν_{18}	0.0757	0.0744	
ν_{eff}	0.0954	0.1498	
I.P.		9.48	11.57

2.2 C_6H_6^+ system

Benzene molecule consists of five electronic states,⁶⁰ namely $\tilde{X}^2 E_{1g}$, $\tilde{B}^2 E_{2g}$, $\tilde{C}^2 A_{2u}$, $\tilde{D}^2 E_{1u}$ and $\tilde{E}^2 B_{2u}$ which produce eight potential energy surfaces^{57,58} due to the presence of doubly degeneracy in $\tilde{X}^2 E_{1g}$, $\tilde{B}^2 E_{2g}$ and $\tilde{D}^2 E_{1u}$ electronic surfaces. Since we have previously considered^{37,39} the five surfaces of C_6H_6^+ system excluding the degeneracy in $\tilde{X}^2 E_{1g}$, $\tilde{B}^2 E_{2g}$ and $\tilde{D}^2 E_{1u}$ states, the aim of our present dynamical calculation is to explore the workability of *parallelized* TDDVR approach on two realistic model Hamiltonians of benzene radical cation: (a) one includes *four states and nine modes* originated due to the *degeneracy* in $\tilde{X}^2 E_{1g}$ and $\tilde{B}^2 E_{2g}$ surfaces; (b) the other is constituted with *three-states and seven-modes* of degenerate $\tilde{D}^2 E_{1u}$ and non-degenerate $\tilde{B}^2 E_{2g}$ states. We adopt two suitable model Hamiltonians,⁵⁹ which incorporate the symmetry properties of the molecule with an expectation to reproduce the PE spectra of the C_6H_6^+ and to provide the explanation of ultrafast relaxation processes from its' excited states. The explicit expression of the four-state nine-mode model Hamiltonian including *degenerate* $\tilde{X}^2 E_{1g}$ and $\tilde{B}^2 E_{2g}$ state is:

$$\hat{H} = (\hat{T}_N + \hat{V}_0)\mathbf{1} + \begin{pmatrix} E_X + \sum_{i=1}^2 \alpha_i^{(X)} Q_i & \sum_{m=15}^{18} \lambda_m^{(X)} Q_y & 0 & \sum_{j=7}^8 \lambda_j^{(XB)} Q_j \\ + \sum_{m=15}^{18} \lambda_m^{(X)} Q_x & & & \\ \sum_{m=15}^{18} \lambda_m^{(X)} Q_y & E_X + \sum_{i=1}^2 \alpha_i^{(X)} Q_i & -\sum_{j=7}^8 \lambda_j^{(XB)} Q_j & 0 \\ -\sum_{m=15}^{18} \lambda_m^{(X)} Q_x & & & \\ 0 & -\sum_{j=7}^8 \lambda_j^{(XB)} Q_j & E_B + \sum_{i=1}^2 \alpha_i^{(B)} Q_i & \sum_{m=15}^{18} \lambda_m^{(B)} Q_y \\ & & + \sum_{m=15}^{18} \lambda_m^{(B)} Q_x & \\ \sum_{j=7}^8 \lambda_j^{(XB)} Q_j & 0 & \sum_{m=15}^{18} \lambda_m^{(B)} Q_y & E_B + \sum_{i=1}^2 \alpha_i^{(B)} Q_i \\ & & & -\sum_{m=15}^{18} \lambda_m^{(B)} Q_x \end{pmatrix}. \quad (4)$$

The two terms $\hat{T}_N$ and $\hat{V}_0$ are as usual KE and PE operators, whereas $\mathbf{1}$ presents the 4×4 unit matrix. The quantities E_k ($k = \tilde{X}, \tilde{B}$) indicate the vertical IP of the corresponding electronic states as presented in table 2 with the frequency values and coupling constants. It is important to note that although the present system consists of two surfaces with six modes, it becomes a *four-state nine-mode Hamiltonian* due to the presence of degeneracy. In this system, the totally symmetric modes (ν_1, ν_2) act as tuning modes, whereas the $\lambda_i^{(X)}$ and $\lambda_i^{(B)}$ represent the linear JT coupling constants. We have used the effective coupling constant (λ_{eff}) and frequency (ω_{eff}) instead of two individual constants, λ_7 and λ_8 and frequencies, ω_7 and ω_8 employing the relations,⁵⁹ $\lambda_{\text{eff}} = \sqrt{\lambda_7^2 + \lambda_8^2}$ and $\omega_{\text{eff}} = (\lambda_7^2 \omega_7 + \lambda_8^2 \omega_8) / (\lambda_7^2 + \lambda_8^2)$, respectively to reduce the computational effort. Here Q denotes the dimensionless normal coordinates of neutral ground state characterized by subscripts x and y for doubly degenerate modes. Our further dynamical calculation is involved with a degenerate electronic surface ($\tilde{D}^2 E_{1u}$) and a non-degenerate one ($\tilde{E}^2 B_{2u}$) in the model Hamiltonian introduced by Köppel *et al*⁵⁹ as:

$$\hat{H} = (\hat{T}_N + \hat{V}_0)\mathbf{1} + \begin{pmatrix} E_D + \sum_{i=1}^2 \alpha_i^{(D)} Q_i & \sum_{m=15}^{18} \lambda_m^{(D)} Q_y & \sum_{j=15}^{18} \lambda_m^{(DE)} Q_j \\ + \sum_{m=15}^{18} \lambda_m^{(D)} Q_x & & \\ \sum_{m=15}^{18} \lambda_m^{(D)} Q_y & E_D + \sum_{i=1}^2 \alpha_i^{(D)} Q_i & \sum_{j=15}^{18} \lambda_m^{(DE)} Q_j \\ -\sum_{m=15}^{18} \lambda_m^{(D)} Q_x & & \\ \sum_{m=15}^{18} \lambda_m^{(DE)} Q_y & \sum_{m=15}^{18} \lambda_m^{(DE)} Q_x & E_E + \sum_{i=1}^2 \alpha_i^{(E)} Q_i \end{pmatrix}. \quad (5)$$

E_k ($k = \tilde{D}, \tilde{E}$) denotes the vertical IP of the corresponding electronic states, whereas $\mathbf{1}$ presents the 3×3 unit matrix. The relevant *ab initio* calculated⁵⁹ coupling constants, frequency values and vertical IP values are presented, where the frequencies are from an MP2 force field calculation for the neutral ground state, coupling constants and IPs from *ab initio* Greens function results. All quantities presented in

tables 2 and 3 are in electron Volt unit. Although the present system consists of two surface with four modes, it becomes a *three-state seven-mode system* due to presence of degeneracy. Here, only the totally symmetric mode (ν_2) acts as tuning mode, whereas the JT active modes (ν_{16} , ν_{17} , ν_{18}) are also play as pseudo Jahn–Teller (PJT) active ones.

In all the systems, the nuclear coordinates are considered as the dimensionless mass-frequency-scaled normal modes with equilibrium geometry of the neutral system at $Q_0 = 0$, where Q is the vector of all vibrational coordinates, $[Q_i = (x_i - x_i^{eq}) (mw_i)^{-1/2}]$, $\hbar = 1$ with ω_i (see tables 1–3), the vibrational frequency of the i th normal mode.

3. The theoretical background of TDDVR approach

Since the detailed formulations of the different versions of TDDVR approach were presented elsewhere,^{28–39} in order to bring the completeness of this article, we briefly demonstrate the relevant equations used for current perspective in the simplest but completely generalized way. The scheme propagates the DVR grid-points by utilizing the ‘classical’ equation of motion with a time-independent width parameter in the primitive basis set. Considering the Hamiltonians for NO_2^- and C_6H_6^+ , the TDSE in the diabatic representation is given by:

$$i\hbar \frac{\partial}{\partial t} \Xi(\{Q_k\}, t) = [\hat{T}_{\{Q_k\}} + \hat{V}(\{Q_k\})] \Xi(\{Q_k\}, t), \quad (6)$$

where

$$\Xi(\{Q_k\}, t) \equiv \begin{pmatrix} \Psi_1(\{Q_k\}, t) \\ \Psi_2(\{Q_k\}, t) \\ \dots \\ \Psi_l(\{Q_k\}, t) \end{pmatrix}, \quad (7)$$

Table 3. The *ab initio* calculated coupling constants, frequencies and vertical IPs used in the dynamical study of C_6H_6^+ using the LVC Hamiltonian (5). All quantities presented below are reproduced from ref. 59.

	ω	$\tilde{D}^2 E_{1u}$	$\tilde{E}^2 B_{2u}$
ν_2	0.1257	0.0705	0.1846
ν_{16}	0.2055	0.1032	0.1701
ν_{17}	0.1497	0.0579	0.1288
ν_{18}	0.0757	0.1755	0.0417
I.P.		14.31	14.61

with $\int \Xi^\dagger(\{Q_k\}, t) \Xi(\{Q_k\}, t) \prod_{k=1}^p dQ_k = 1$ at any time t . In case of NO_2^- , l goes from 1 to 2 and for C_6H_6^+ , l varies from 1 to either 3 or 4.

The l th diabatic wavefunction $[\Psi_l(\{Q_k\}, t)]$ for many DOF (p) is expanded in terms of products of TDDVR basis functions $[\{\psi_{i_k}(Q_k, t)\}]$ for the different (k) modes,

$$\Psi_l(\{Q_k\}, t) = \sum_{i_1 i_2 \dots i_p} c_{i_1 i_2 \dots i_p, l}(t) \prod_{k=1}^p \psi_{i_k}(Q_k, t), \quad (8)$$

and the i_k th basis for the k th mode is again expressed with DVR basis multiplied by plane wave to represent the coordinate, Q_k , as a function of time, t ,

$$\begin{aligned} \psi_{i_k}(Q_k, t) &= \phi(Q_k, t) \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) \xi_n(x_k) \\ &= \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) \Phi_n(Q_k, t), \\ \phi(Q_k, t) &= \pi^{1/4} \exp\left(\frac{i}{\hbar} \{P_{Q_k^c}(t)[Q_k - Q_k^c(t)]\}\right), \end{aligned} \quad (9)$$

where harmonic oscillator eigenfunctions are the primitive basis to construct DVR functions,

$$\begin{aligned} \xi_n(x_k) &= \left(\frac{2ImA_k}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!2^n\sqrt{\pi}}} \exp(-(x_k)^2/2) H_n(x_k), \\ x_k &= \sqrt{\frac{2ImA_k}{\hbar}} (Q_k - Q_k^c(t)), \\ x_{i_k} &= \sqrt{\frac{2ImA_k}{\hbar}} (Q_{i_k}(t) - Q_k^c(t)). \end{aligned} \quad (10)$$

A TDDVR grid-point, Q_{i_k} , is determined by (10) using the root, x_{i_k} , of N_k th Hermite polynomial, $H_{N_k}(x_k)$. Although the roots (x_{i_k} s) of the polynomial are fixed values but the positions of the TDDVR grid-points (Q_{i_k} s) will change as a function of time due to the time-dependent variables, $Q_k^c(t)$,

$$Q_{i_k}(t) = Q_k^c(t) + \sqrt{\frac{\hbar}{2ImA_k}} x_{i_k}. \quad (11)$$

The Gauss–Hermite basis, $\Phi_n(Q_k, t)$, for the k th mode as introduced in (9) have the following important properties: (a) they form an orthonormal basis,

$$\int dQ_k \Phi_m^*(Q_k, t) \Phi_n(Q_k, t) = \delta_{mn}^k, \quad (12)$$

(b) the ground state of the GH basis is a Gaussian Wave Packet.

The TDDVR basis functions, ψ_{i_k} s, as defined in (8) for the k th mode constitute an orthogonal but not normalized set,

$$\int dQ_k \psi_{i_k}^*(Q_k, t) \psi_{i'_k}(Q_k, t) = \delta_{i_k i'_k} A_{i_k i'_k}, \quad (13)$$

where A_k is the normalization factor.

When the model Hamiltonian [(1) or (4) or (5)] and the TDDVR representation of wavefunction (7)–(10) are substituted into the TDSE (6), the classical path picture appears naturally along with the quantum equation of motion. The time-dependent variational theory provides the compact form of TDDVR matrix equation for quantum motion on the l th PES as given below,

$$i\hbar \dot{\mathbf{C}}_l = \mathbf{H}_{ll}^t \mathbf{C}_l + \mathbf{A} \sum_{l' \neq l} \mathbf{V}_{ll'} \mathbf{C}_{l'}, \quad (14)$$

and the matrix equation under a similarity transformation takes the following convenient form,

$$i\hbar \dot{\mathbf{D}}_l(t) = \mathbf{A}^{-1/2} \mathbf{H}_{ll}^t \mathbf{A}^{-1/2} \mathbf{D}_l + \sum_{l' \neq l} \mathbf{V}_{ll'} \mathbf{D}_{l'}, \quad (15)$$

where $\mathbf{D}_l = \mathbf{A}^{1/2} \mathbf{C}_l$ and $l = 1, 2, 3, 4$.

The explicit expression of the differential equation for an amplitude, $d_{i_1 i_2 \dots i_p, l}$ on the l th surface is,

$$\begin{aligned} i\hbar \dot{d}_{i_1 i_2 \dots i_p, l} = & \frac{1}{2} \left\{ \sum_k \dot{P}_{Q_k^c} \sqrt{\frac{\hbar}{ImA_k}} \bar{X}_{i_k i_k} \right\} d_{i_1 i_2 \dots i_p, l} \\ & + \left\{ \sum_k \frac{\mu(\dot{Q}_k^c)^2}{2} \right\} d_{i_1 i_2 \dots i_p, l} \\ & + V_{ll}(i_1 i_2 \dots i_p) d_{i_1 i_2 \dots i_p, l} + \sum_{l' \neq l} V_{ll'}(i_1 i_2 \dots i_p) d_{i_1 i_2 \dots i_p, l'} \\ & + \sum_k \left\{ \frac{\hbar ImA_k}{2\mu} \sum_{i'_1 i'_2 \dots i'_p} \{2\bar{Y}_{i_k i'_k} - \bar{Z}_{i_k i'_k}\} d_{i'_1 i'_2 \dots i'_p, l} \prod_{k' \neq k}^p \delta_{i_k i'_k} \right\}, \quad (16) \end{aligned}$$

where the explicit form of the matrices used in quantum equation of motion are presented as follows:

$$\begin{aligned} \bar{X}_{i_k i'_k} &= \frac{X_{i_k i'_k}}{\sqrt{A_{i_k i_k} A_{i'_k i'_k}}}, \quad \bar{Y}_{i_k i'_k} = \frac{Y_{i_k i'_k}}{\sqrt{A_{i_k i_k} A_{i'_k i'_k}}}, \\ \text{and } \bar{Z}_{i_k i'_k} &= \frac{Z_{i_k i'_k}}{\sqrt{A_{i_k i_k} A_{i'_k i'_k}}}, \end{aligned}$$

$$d_{i_1 i_2 \dots i_p, l} = c_{i_1 i_2 \dots i_p, l} \prod_{k=1}^p (A_{i_k i_k})^{1/2},$$

$$A_{i_k i'_k} = \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) \xi_n(x_{i'_k}),$$

$$X_{i_k i'_k} = \sum_{n=0}^{N_k-1} \xi_{n+1}^*(x_{i_k}) \sqrt{n+1} \xi_n(x_{i'_k}) + \sum_{n=1}^{N_k} \xi_{n-1}^*(x_{i_k}) \sqrt{n} \xi_n(x_{i'_k}),$$

$$Y_{i_k i'_k} = \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) 2n \xi_n(x_{i'_k}),$$

$$Z_{i_k i'_k} = \sum_{n=0}^{N_k-2} \xi_{n+2}^*(x_{i_k}) \sqrt{(n+1)(n+2)} \xi_n(x_{i'_k})$$

$$+ \sum_{n=2}^{N_k} \xi_{n-2}^*(x_{i_k}) \sqrt{n(n-1)} \xi_n(x_{i'_k})$$

$$+ \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) (2n+1) \xi_n(x_{i'_k}). \quad (17)$$

The TDDVR equation of motion for quantum dynamics has the following important characteristics: (a) the component matrices ($\{\mathbf{A}_k\}$, $\{\mathbf{X}_k\}$, $\{\mathbf{Y}_k\}$, $\{\mathbf{Z}_k\}$) of the TDDVR Hamiltonian [see (16)] are time-independent and need to be evaluated once for all; (b) Since the matrices, $\{\mathbf{X}_k\}$, are diagonal and associated with the ‘classical’ variables $\{\dot{P}_{Q_k^c}(t)\}$, the non-linear dynamics of these ‘classical’ quantities affects the convergence but not the final solution of the quantum equations of motion; (c) as the off-diagonal elements of $\{\mathbf{Y}_k\}$ and $\{\mathbf{Z}_k\}$ matrices couple the grid-points and dominate the quantum dynamics, any non-linear ‘classical’ propagation of their associated parameters, $\{ImA_k\}$, is not desirable, and hence, a time-independent $\{ImA_k\}$ is the obvious choice. The contribution of different modes on a time-dependent amplitude ($\dot{d}_{i_1 i_2 \dots i_p, l}$) is evaluated independently, i.e. $\mathbf{Y}_k$ and $\mathbf{Z}_k$ matrices couple grid-points or basis functions of the k th mode only. Such multiplications along with the calculations on each

surface demand an obvious parallelization of the algorithm reducing computational time remarkably and motivate us for persuading relatively large dimensional calculations.^{37,39}

Moreover, the classical path equations for the k th mode, those appear along with the quantum equation of motion, can be written as

$$\dot{Q}_k^c(t) = \frac{P_{Q_k^c}(t)}{\mu}, \quad (18)$$

$$\dot{P}_{Q_k^c}(t) = -\frac{dV(\{Q_k\})}{dQ_k} \Big|_{Q_k(t)=Q_k^c(t)} + Q_k^F(t), \quad (19)$$

where $Q_k^F(t)$ is the quantum force for the k th mode. A rigorous expression of $Q_k^F(t)$ is derived by using Dirac–Frenkel variational principle,⁶¹ i.e. by minimizing the following integral with respect to $\hat{P}_{Q_k^c}$,

$$I = \int \left(-i\hbar \frac{\partial \Xi^*(\{Q_k\}, t)}{\partial t} - H(\{P_{Q_k}\}, \{Q_k\}) \Xi^*(\{Q_k\}, t) \right) \times \left(i\hbar \frac{\partial \Xi(\{Q_k\}, t)}{\partial t} - H(\{P_{Q_k}\}, \{Q_k\}) \Xi(\{Q_k\}, t) \right) \prod_{k=1}^p dQ_k. \quad (20)$$

The explicit expression of $Q_k^F(t)$ thus obtained is

$$Q_k^F(t) = \sum_l \sum_{i_1 i_2 \dots i_k \dots i_p} c_{i_1 i_2 \dots i_k \dots i_p, l}^*(t) c_{i_1 i_2 \dots i_k \dots i_p, l}(t) \times \left[\frac{2(ImA_k)^2}{\mu} \left[S_{i_k i_k'}^{(2)*} \frac{S_{i_k i_k}^{(1)*}}{A_{i_k i_k}} - S_{i_k i_k'}^{(3)} \right] - \frac{\hbar ImA_k}{\mu} \left[R_{i_k i_k'}^{(1)*} \frac{S_{i_k i_k}^{(1)*}}{A_{i_k i_k}} - T_{i_k i_k'}^* \right] \right] \Bigg/ \left[\sum_l \sum_{i_1 i_2 \dots i_k \dots i_p} c_{i_1 i_2 \dots i_k \dots i_p, l}^*(t) c_{i_1 i_2 \dots i_k \dots i_p, l}(t) \frac{S_{i_k i_k}^{(1)*} S_{i_k i_k}^{(1)}}{A_{i_k i_k}} - \sum_l \sum_{i_1 i_2 \dots i_k \dots i_p} c_{i_1 i_2 \dots i_k \dots i_p, l}^*(t) c_{i_1 i_2 \dots i_k \dots i_p, l}(t) S_{i_k i_k'}^{*(2)} \right]. \quad (21)$$

The explicit form of R , $S^{(n)}$ and T matrices are

$$R_{i_k i_k'} = \sum_p \xi_p^*(x_{i_k}) \xi_p(x_{i_k'}) 2p,$$

$$S_{i_k i_k'}^{(n)} = \sum_{pq} \xi_p^*(x_{i_k}) \xi_q(x_{i_k'}) \int \Phi_q^*(Q_k, t) (Q_k - Q_k^c(t))^n \Phi_p(Q_k, t) dQ_k, \quad (22)$$

$$T_{i_k i_k'} = \sum_{pq} \xi_p(x_{i_k}) \xi_q^*(x_{i_k'}) 2p \int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t)) \Phi_q(Q_k, t) dQ_k,$$

with

$$\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t)) \Phi_q(Q_k, t) dQ_k = \frac{1}{2} \sqrt{\frac{\hbar}{ImA_k}} \{ \sqrt{p+1} \delta_{p+1, q} + \sqrt{p} \delta_{p-1, q} \},$$

$$\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t))^2 \Phi_q(Q_k, t) dQ_k = \frac{\hbar}{4ImA_k} \times \{ \sqrt{(p+1)(p+2)} \delta_{p+2, q} + (2p+1) \delta_{p, q} + \sqrt{p(p-1)} \delta_{p-2, q} \},$$

$$\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t))^3 \Phi_q(Q_k, t) dQ_k = \frac{1}{8} \left(\frac{\hbar}{ImA_k} \right)^{3/2} \times \{ \sqrt{(p+1)(p+2)(p+3)} \delta_{p+3, q} + 3(p+1) \sqrt{p+1} \delta_{p+1, q} + 3p \sqrt{p} \delta_{p-1, q} + \sqrt{p(p-1)(p-2)} \delta_{p-3, q} \}. \quad (23)$$

The matrices, R , $S^{(n)}$ and T are time-independent and need to be calculated once for all the time. It is important to note that the time-dependence of Q_k^F arises from the coefficients $\{c_{i_1 i_2 \dots i_k \dots i_p, l}(t)\}$ only.

4. Initialization and propagation

Since the intramolecular relaxation and the effects due to CI are post excitation phenomena, a vertical excitation is assumed at the FC point ($Q = 0$) just before initiating the dynamics so that the wavefunction at $t = 0$ on the upper electronic state is same as that for the lowest state ($\tilde{X}^2 A_1$ state for NO_2 ,

$\tilde{X}^2 E_{1g}$ or $\tilde{D}^2 E_{1u}$ state for $C_6H_6^+$). Thus, the initial wavefunction for any upper electronic state is a product of Gaussian functions ($\{\Phi_{GWP}(Q_k)\}$) centered around the equilibrium geometry ($Q_0 = 0$). In order to specify the initial amplitude vector, $\mathbf{d}$ (16), multi-dimensional TDDVR wavefunction is equated with the product of $\Phi_{GWP}(Q_k)$ functions,

$$\begin{aligned} \prod_{k=1}^p \Phi_{GWP}(Q_k) &= \sum_{i_1 i_2 \dots i_p} c_{i_1 i_2 \dots i_p} \prod_{k=1}^p \psi_{i_k}(Q_k, t) \\ &= \sum_{i_1 i_2 \dots i_p} c_{i_1 i_2 \dots i_p} \prod_{k=1}^p \sum_{n=0}^{N_k} \xi_n(x_{i_k}) \Phi_n(Q_k). \end{aligned} \quad (24)$$

Using the property of the TDDVR basis,

$$\psi_{i_k}(Q_k, t) = \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) \Phi_n(Q_k, t) \approx \delta(Q_k - Q_{i_k}), \quad (25)$$

(24) takes the following form,

$$\begin{aligned} \prod_{k=1}^p \Phi_{GWP}(Q_k) &= c_{i_1 i_2 \dots i_p} \prod_{k=1}^p \sum_{n=0}^{N_k} \xi_n(x_{i_k}) \Phi_n(Q_k) \\ &= c_{i_1 i_2 \dots i_p} \prod_{k=1}^p A_{i_k}. \end{aligned} \quad (26)$$

We rearrange (26) as below to define the vector d_l on the upper surface ($\tilde{A}^2 B_2$ state for NO_2 and $\tilde{B}^2 E_{2g}$ or $\tilde{E}^2 B_{2u}$ state for $C_6H_6^+$),

$$d_{i_1 i_2 \dots i_p, l} = c_{i_1 i_2 \dots i_p} \prod_{k=1}^p A_{i_k} = \frac{\prod_{k=1}^p \Phi_{GWP}(Q_{i_k})}{\sqrt{\prod_{k=1}^p A_{i_k}}}, \quad (27)$$

where the initial expansion coefficient vector d_l on the lower surface is,

$$d_{i_1 i_2 \dots i_p, l'} = 0, l' \neq l. \quad (28)$$

The width parameters ($\{ImA_k\}$) of the Gaussian functions ($\{\Phi_{GWP}(Q_k)\}$) are defined by the frequencies ($\{\omega_k\}$) of the respective normal modes. The dynamical evolution of the system is being performed by simultaneously solving the set of differential

(16), (18) and (19). Since $\mathbf{d}$ vectors are defined at the grid points, the probability of finding the system on a particular diabatic surface is obtained by mere grid-summation,

$$P_l(t) = \sum_{i_1 i_2 \dots i_p} |d_{i_1 i_2 \dots i_p, l}|^2, l=1, 2, \dots \quad (29)$$

In order to calculate adiabatic population on a particular surface, diabatic amplitude vector ($\mathbf{d}$) is transformed to the adiabatic ($\mathbf{e}$) one,

$$\mathbf{e} = \mathbf{T}^\dagger \mathbf{d}, \quad (30)$$

where the $\mathbf{T}$ matrix defines the transformation of diabatic ($\mathbf{V}$) to adiabatic ($\mathbf{U}$) PES matrices, $\mathbf{U} = \mathbf{T}^\dagger \mathbf{V} \mathbf{T}$.

5. Analysis of the spectra and nuclear densities

The TDDVR method is used to propagate the nuclear wavefunction and thereby, to calculate the autocorrelation function $[C(t)]$ where the Fourier transform of $C(t)$ gives photodetachment spectra of the NO_2 and various PE bands of $C_6H_6^+$:

$$I(\omega) \propto \omega \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt, \quad (31)$$

where

$$C(t) = \langle \Psi(t) | \Psi(0) \rangle \quad (32)$$

$$= \left\langle \Psi^* \left(\frac{t}{2} \right) \middle| \Psi \left(\frac{t}{2} \right) \right\rangle. \quad (33)$$

Equation (33)⁶² is more accurate, computationally faster and convenient to implement than the previous (32). On the other hand, (33) is valid only if the initial wavefunction is real and the Hamiltonian is symmetric.⁶³ Since the experimental spectral lines due to the resolution of the spectrometer appear broadened, one can incorporate this effect to the calculated spectra by convoluting with a suitable peaked curve. In the time-dependent picture, this phenomenological broadening is equivalent to damping the autocorrelation function by a time-dependent function as chosen below:

$$h(t) = \exp \left[- \left(\frac{|t|}{\tau} \right)^2 \right], \quad (34)$$

with an appropriate parameter, τ . Though the experimental broadening of a spectrum along requires a large value of τ , the calculated spectrum of NO_2^- and the PE bands of C_6H_6^+ are in agreement with the experimental ones.

Moreover, as the propagation of wavefunction and the calculated autocorrelation function is up to a finite time, artifacts known as Gibbs phenomenon⁶⁴ develop in the spectrum. It can be reduced by multiplying the autocorrelation with the following function,

$$g(t) = \cos^n \left(\frac{\pi t}{2T} \right), \quad (35)$$

where n is an integer number which is set to 2 in this work and T is the length of propagation. This function convolutes the spectrum with,

$$\tilde{g}(\omega) = \frac{4\pi T}{\pi^2 - (2\omega T)^2} \cos(\omega T), \quad (36)$$

such that $C(t)$ is smoothened to zero.

In this numerical calculation, one of the electronic states, $\tilde{X}^2A_1$ or $\tilde{A}^2B_2$ of NO_2 is populated by locating an initial wave packet, $\Psi(0)$ and the propagation of the corresponding wave packet ($\Psi(t)$) is then carried out to obtain the corresponding autocorrelation function, where its Fourier transformation (31)⁶³ leads to the individual state spectra. Since the total photodetachment spectra of NO_2^- is very complex (see the upper panel of figure 1) and originates due to the contributions of two electronic states, we calculate two electronic state band separately and convolute them with proper weight to obtain the entire spectra. For C_6H_6^+ , we perform numerical calculations starting with an initial wave packet $\Psi(0)$ from the electronic state X^2E_{1g} for Hamiltonian (4), whereas D^2E_{1u} and E^2B_{2u} states for Hamiltonian (5). The numerical propagation of $\Psi(t)$ is then performed to obtain the corresponding spectra according to equation (31).

We also focused on the diabatic reduced densities,⁶⁰ $\rho_l(Q_i, Q_j, t)$ of the wave packet on different potential energy surfaces $l = \tilde{X}, \tilde{A}$, of NO_2 as defined below:

$$\rho_l(Q_i, Q_j, t) = \int \Psi_l^*(\{Q_i\}, t) \Psi_l(\{Q_j\}, t) \Pi_{k \neq i, j} dQ_k, \quad (37)$$

where Ψ_l is the component of the total wave function Ξ , i.e. $\Xi = (\Psi_X, \Psi_A)$.

Figure 1. (a) Presents the experimental low resolution (in 266 nm) photodetachment spectrum⁴⁵ of NO_2^- , whereas (b) and (c) display the theoretical results obtained by using Lanczos algorithm⁶⁵ and TDDVR method, respectively. The TDDVR calculated theoretical result is obtained with low damping parameter value ($\tau = 2.0$).

Table 4. The optimum number of TDDVR basis functions used in the present dynamical calculation.

System	Initial wave function located at	Normal modes	TDDVR basis
NO_2^-	$\tilde{A}^2B_2$	ν_1, ν_2, ν_3	35, 34, 21
C_6H_6^+ ($\tilde{X}^2E_{1g} - \tilde{B}^2E_{2g}$)	$\tilde{B}^2E_{2g}$	$\nu_1, \nu_2, \nu_{\text{eff}}$ $\nu_{15x}, \nu_{15y}, \nu_{16x}$ $\nu_{16y}, \nu_{17x}, \nu_{17y}$ ν_{18x}, ν_{18y}	3, 9, 9 1, 1, 9 9, 3, 3 9, 9
C_6H_6^+ ($\tilde{D}^2E_{1u} - \tilde{E}^2B_{2u}$)	$\tilde{D}^2E_{1u}$	$\nu_2, \nu_{16x}, \nu_{16y}$ $\nu_{17x}, \nu_{17y}, \nu_{18x}$ ν_{18y}	13, 9, 9 9, 9, 13 13

6. The numerical details

Since the model Hamiltonian (1) of the NO_2 system is composite of two electronic surfaces ($\tilde{X}^2A_1$ and $\tilde{A}^2B_2$) and three important vibrationally active modes (ν_1, ν_2 and ν_3), we treat them utilizing TDDVR methodology to simulate the photodetachment spectra of NO_2^- and reveal the internal feature of population dynamics. The number of TDDVR basis used to perform dynamics of NO_2^- are presented in table 4. In the present system, although the TDDVR grid points, $N_{\nu_1} = 30$, $N_{\nu_2} = 25$ and $N_{\nu_3} = 12$ are sufficient to yield a converged spectrum, we have used total 24990 TDDVR basis sets/gridpoints, i.e. the numbers of TDDVR grid-points used to perform the dynamical calculation are: $N_{\nu_1} = 35$, $N_{\nu_2} = 34$ and $N_{\nu_3} = 21$.

The optimum numbers of TDDVR grid-points used to perform the dynamics on *four-surface nine-mode* Hamiltonian (4) of C_6H_6^+ locating the initial wave function on $\tilde{B}^2E_{2g}$ state are presented in table 4. Since the ν_{15} mode has a negligible effect in the dynamics, we have treated it classically in this current calculation. Similarly, the numbers of TDDVR grid-points used to perform the dynamics on Hamiltonian (5) are displayed in table 4. TDDVR formulation is such that with the sufficient number of grid-points, the calculated results appear as independent of the initial choice of ‘classical’ momentum of the central trajectory and thereby, we have chosen $Q_i(t_0) = 0$ and $P_i(t_0) = 0$ for those modes. On the other hand, this choice plays a key role when a mode is treated at the classical limit (a single grid-point) or at near classical limit (few grid-points) because the dynamics is solely or essentially dictated by classical mechanics. In the present calculations, the

choice of classical parameters for one grid-point dynamics are $Q_i(t_0) = 0$ and $P_i(t_0) = \sqrt{\hbar m \omega_i}$.

We calculate the quality of the results by estimating the magnitude of the error due to the use of finite TDDVR basis in the autocorrelation function,

$$\Delta(t) = |\langle \Psi(0) | \Psi(t) \rangle - \langle \Psi'(0) | \Psi'(t) \rangle|^2, \quad (43)$$

where $\Psi'(t)$ is the wavefunction ignoring the least populated TDDVR basis function. It is observed in the current dynamical calculation that the change of autocorrelation function, $\Delta(t)$, in the model remains below 10^{-3} on addition or subtraction of a TDDVR basis in a particular mode.

7. Results and discussion

The focus of our current investigation is to calculate (a) the autocorrelation function followed by the photodetachment spectra of NO_2^- , and (b) the reduced density with ‘classical’ trajectories to demonstrate its’ nuclear population dynamics in detail. The NO_2^- Hamiltonian for two electronic states only with first order coupling is considered for broad band spectrum, whereas we perform dynamical calculation on full second order vibronic coupling realistic model Hamiltonian to simulate better resolved one. On the other hand, in order to calculate the PE spectra of benzene molecule, we have performed the dynamics on the corresponding multi-surface, multi-mode vibronically coupled model Hamiltonian of C_6H_6^+ with *degenerate* states by using a parallelized algorithm of TDDVR approach. We explore the agreement of our calculated spectrum both with the

experimentally measured as well as other theoretically calculated profiles.

7.1 NO_2^- system

7.1a Calculation of spectra: Since it is well established that the low and high energy region of the experimental PE spectrum⁴⁵ of NO_2^- (see figure 1a) originate due to separate contributions of the ground ($\tilde{X}^2A_1$) and first excited ($\tilde{A}^2B_2$) electronic state, respectively, we perform dynamics locating the initial

wave function separately on those states and finally convolute those individual bands with equal weight factor and low damping parameter value ($\tau = 2.71$) to obtain the corresponding spectra of the molecule as displayed in figure 1c in comparison with the result obtained by standard Lanczos algorithm⁶⁵ (figure 1b). It is quite obvious from the figure 1 that our theoretically calculated (TDDVR) spectra shows peak by peak correspondence with the experimental spectrum along with the envelop obtained by Mahapatra *et al.*⁵⁰ Although Weaver *et al.*⁴⁵ experimentally

Figure 2. The $\tilde{A}^2B_2$ PE band of NO_2^- is obtained due to photodetachment of NO_2^- for three different *ab initio* calculated λ values 0.0, 0.087 and 0.28 in the panels (a), (b) and (c), respectively.

Figure 3. (a) Presents the experimental better resolved (351 nm) PE spectrum⁴⁶ of NO_2^- , whereas (b) display the corresponding result obtained from TDDVR methodology using LVC model Hamiltonian with higher damping parameter value ($\tau = 4.5$). On the other hand, (c) presents the PE spectra obtained by using bilinear and quadratically coupled Hamiltonian.

measured PE spectra of NO_2^- using 266 nm (4.66 eV) pulsed Nd : YAG laser beam to indicate the two full $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ bands with partial $\tilde{C}^2A_2$ spectrum but for feasible theoretical calculation, we include two lowest energetic states to simulate corresponding spectra. The experimental spectrum (see figure 1a) shows the intensity of the ejected electron (in arbitrary units) as function of the internal energy of the final vibronic state rather than plotting intensity verses KE of the ejected electron in the usual PE spectra. These two are related as: $E_k = h\nu - \text{EA} - E_v$, where E_k = electron KE, $h\nu$ = energy of the laser photon, EA = electron affinity of NO_2 and E_v = internal energy of the final vibrational state. We demonstrate the effect of *ab initio* calculated⁵⁰ three λ values (0.0, 0.087 and 0.28) on the $\tilde{A}^2B_2$ spectral profile as shown in figure 2a–c, where both the calculations (present and MCTDH) for PE spectra (see figure 2b) with $\lambda = 0.087$ show the best agreement with the experimental one. Heller *et al*[66] previously considered $\lambda = 0.28$ to study $\tilde{X}^2A_1 \rightarrow \tilde{A}^2B_2$ adsorption process from the available *ab initio* literature data.⁶⁷ It can be seen that $\tilde{A}^2B_2$ band is well resolved than the $\tilde{X}^2A_1$ band at a particular laser energy (4.66 eV) in which the experimental measurement has been made.

Ervin *et al*⁴⁶ experimentally measured the PE spectra of NO_2^- with better resolution (351 nm) argon ion laser by which only $\tilde{X}^2A_1$ state is accessible not the higher excited ones, viz. $\tilde{A}^2B_2$, $\tilde{C}^2A_2$. We have theoretically calculated this spectra using the *ab initio* calculated data (see table 1) with higher damping parameter ($\tau = 4.5$) value and presented along with the experimental one measured by Ervin *et al*⁴⁶ in figures 3a and b, respectively. For better simulation of experimental $\tilde{X}^2A_1$ band, we consider the quadratic and bilinear expansion terms⁵⁰ of the same Hamiltonian (1) with a' , b' instead of a , b , which include the Duschinsky rotation⁶⁸ of two symmetric modes (ν_1 , ν_2) due to the neutral to anionic normal mode transformation.⁶⁹ Similar to Ervin *et al*⁴⁶ approach, we assume the vibrational frequencies of the neutral NO_2 and that of anion are the same. We have considered the second order expansion⁷⁰ of the parameters, a and b , which are denoted by a' and b' , respectively, of the Hamiltonian (1) with $\beta_1^{(1)} = 0.274$ eV, $\beta_2^{(2)} = 0.240$ eV, $\gamma_{11} = 1.250 \times 10^{-3}$ eV, $\gamma_{12} = 1.194 \times 10^{-2}$ eV, $\gamma_{22} = 1.376 \times 10^{-3}$ eV and the vertical IP as 1.1 eV. The theoretically calculated $\tilde{X}^2A_1$ band obtained by considering $\lambda = 0$ is also compared with the band produced by adopting

the coupling parameter as listed in table 1. The identical results demonstrate the negligible effect of coupling on $\tilde{X}^2A_1$ band. Our theoretical spectral envelop with quadratic and bilinear terms is presented in figure 3c along with experimental one (figure 3a). It is worthwhile to mention that all the theoretically calculated (TDDVR) spectral profiles show satisfactory agreement with the results obtained from experiment^{45,46} and Mahapatra *et al*.⁵⁰

7.1b ‘Classical’ trajectory and nuclear population dynamics: The present segment of our discussion is enriched with a detailed nuclear population dynamics on two electronic states ($\tilde{X}^2A_1 - \tilde{A}^2B_2$) considering the general Hamiltonian (1) locating the initial wave function on $\tilde{A}^2B_2$ electronic state at FC point and present the corresponding population profiles in figure 4, where the dashed (blue) line and solid (red) line display the $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ state population, respectively, as functions of time. Moreover, we have demonstrated the diabatic reduced densities ($\rho_i(Q_i, Q_j, t)$) of the time-dependent wave function initially locating the wave packet on the same upper electronic surface, $\tilde{A}^2B_2$. It may be important to mention that the ν_1 and ν_2 modes play a crucial role to obtain the desire population dynamics, reproduce the experimental spectra and the reduced density plots on the $\{Q_1, Q_2\}$ plane become interesting to observe. The ‘classical’ trajectories ($Q_1(t)$ and $Q_2(t)$) for the ν_1 and ν_2 modes and the corresponding energy functional ($E(Q_1(t), Q_2(t))$)

Figure 4. Displays the population profile of NO_2 while performing time-dependent dynamics with an initial wave packet located on $\tilde{A}^2B_2$ electronic surface at Frank-Condon point, $Q = 0$.

Figure 5. (a) Presents the classical trajectories, $Q_1(t)$ and $Q_2(t)$, for the modes ν_1 and ν_2 on the $\tilde{X}^2A_1$ state, whereas the corresponding energy functional, $E(Q_1(t), Q_2(t))$, is presented in (b). The panels (c)–(h) present the diabatic reduced densities of NO_2 while performing calculation with an initial wave packet located on $\tilde{A}^2B_2$ state at FC point, $Q = 0$. The panel (c) displays the reduced density at $t = 10$ fs on $\tilde{A}^2B_2$ surface, whereas the panels (d)–(h) for $t = 11$, 31, 55, 210 and 310 fs on $\tilde{X}^2A_1$ electronic surface, respectively. The diagonal solid lines in the panel (c)–(h) indicate the seam of CIs between two ($\tilde{A}^2B_2 - \tilde{X}^2A_1$) surfaces.

clearly explain the movement of the wavepacket and its nodal structure as functions of time. Panel (a) of figure 5 displays the centers of the wavepackets known as ‘classical’ trajectories ($Q_1(t)$ and $Q_2(t)$) as functions of time, where the panel b of same figure depicts the corresponding energy functional

($E(Q_1(t), Q_2(t))$) calculated by using ‘classical’ equation of motion for the mode ν_1 and ν_2 on the $\tilde{X}^2A_1$ surface. Both the trajectories, $Q_1(t)$ and $Q_2(t)$, move together to the negative direction of the configuration space attaining a minimum value and then, translate back to the positive side with widely

Figure 6. (a) Presents the experimental $\tilde{X}^2E_{1g}$ state PE spectrum of $C_6H_6^+$, whereas (b) and (c) display corresponding theoretical envelop obtained from TDDVR and MCTDH method with ν_{16} , ν_{17} , ν_{18} modes. The same spectra is also calculated using all modes (ν_2 , ν_{16} , ν_{17} and ν_{18}) with TDDVR and MCTDH approach and presented in (d) and (e), respectively.

different numerical magnitude. The filled squares in the ‘classical’ trajectories (figure 5a) or energy functionals (figure 5b) indicate the specific time for the density plots demonstrated in figures 5d–f. The panel c and g–h indicate the density plots at smaller and larger time, respectively, which are not indicated in panel a and b. At this point, we must mention that the density plot in panel c represents the wavepacket on the $\tilde{A}^2B_2$ state and the wavefunction on the $\tilde{X}^2A_1$ surface is presented as density plots in

figures 5d–h. The density of the wavepacket changes its position in accordance with the ‘classical’ trajectories, i.e., the wavepacket moves from the origin ($Q_1 = Q_2 = 0$ at $t = 0$) to the negative region of Q_1 and Q_2 up to a certain time preserving its’ symmetry approximately and then, the density spreads as the separation between the trajectories, $Q_1(t)$ and $Q_2(t)$ increases. At the same time, the change of energy ($E(Q_1(t), Q_2(t))$) as function of time help to understand the nodal structure of the density plots.

As the energy functional (figure 5b) increases, the nodes appear distinctly (figures 5e–f) and then, the density becomes diffuse with complex nodal structure (figures 5g–h) at longer time. The reduced density of time-dependent wave function (in panel d) become shrinked to a small region in the configuration space as indicated by the crossing of the $Q_1(t)$ and $Q_2(t)$ trajectories at ~ 11 fs (in figure 5a) but the density diffuses with nodal structure at ~ 31 fs (in figure 5e) when those trajectories show greater separation (see panel a) from each other with high $E(Q_1(t), Q_2(t))$ value. The step-wise population decay (see figure 4) of $\tilde{A}^2B_2$ state and subsequent increment of the $\tilde{X}^2A_1$ state can be easily understood by the snapshots of figure 5. As the dynamics starts ($t = 0$), the wave packet reaches quickly (< 10 fs) from the initial position ($Q_1 = Q_2 = 0$) to the seam of the CIs (indicated by solid diagonal lines) preserving its symmetry on the $\tilde{A}$ PES and splits into two packets: one remains on the $\tilde{A}$ surface (figure 5c) and other descends also preserving its symmetry on the $\tilde{X}$ surface which can be seen in figure 5d. With the increase of time (> 30 fs), another part of the wave packet descends on the $\tilde{X}$ surface and destroys the symmetry of the existing wave packet (see figure 5e). This step-by-step decay of the wave packet from the $\tilde{A}$ to the $\tilde{X}$ surface is reflected in the decaying population profile of $\tilde{A}$ state (see figure 4). At longer time range, the structure of reduced density becomes very complex, when the $\tilde{X}$ state population gradually increases to attain a maximum value (~ 0.6).

7.2 $C_6H_6^+$ system

7.2a Calculation of spectra: In this section, we discuss the dynamical properties of the four electronic states, namely $\tilde{X}^2E_{1g}$, $\tilde{B}^2E_{2g}$, $\tilde{D}^2E_{1u}$ and $\tilde{E}^2B_{2u}$, of the benzene radical cation. The Hamiltonians ((4) and (5)) are constituted by considering the degeneracy of the states, $\tilde{X}^2E_{1g}$, $\tilde{B}^2E_{2g}$ and $\tilde{D}^2E_{1u}$, where the experimental⁷¹ $\tilde{X}^2E_{1g}$ spectra (see figure 6a) is reproduced by locating the initial wave packet on the corresponding PES at the FC point. We perform the dynamics with two groups of modes: one contains only the JT modes (ν_{16} , ν_{17} , ν_{18}) and the other consists of totally symmetric mode (ν_2) along with the JT ones. The TDDVR calculated spectra obtained by $\nu_{16} + \nu_{17} + \nu_{18}$ and $\nu_2 + \nu_{16} + \nu_{17} + \nu_{18}$ modes are presented in figures 6b and d, where the corresponding spectra⁵⁹ by MCTDH methodology^{72–74}

are displayed in figures 6c and e, respectively. Such broad band TDDVR spectra are calculated with τ value 9.5. On the contrary, we have calculated the better resolved $\tilde{X}^2E_{1g}$ spectra with τ value 28.5 and presented the corresponding spectra in figure 7a along with MCTDH calculated ones in figure 7b. In both panels (figures 7a and b), the solid and dotted line display $\tilde{X}^2E_{1g}$ spectra with and without coupling to $\tilde{B}^2E_{2g}$ state, respectively. The TDDVR calculated theoretical $\tilde{X}^2E_{1g}$ spectra show good agreement with MCTDH calculated⁵⁹ as well as experimental ones.⁷¹

The experimental $\tilde{D}^2E_{1u} - \tilde{E}^2B_{2u}$ band⁷¹ in the PE spectrum of benzene radical cation is composite of two humps and a structureless plateau in between the humps as presented in figure 8a, where the MCTDH calculated individual (dot-dash line for D state and dashed line for E state) and convoluted (solid line) spectra are displayed in figure 8b. Since it has been well established⁵⁵ that the $\tilde{D}^2E_{1u} - \tilde{E}^2B_{2u}$ band is the weighted sum of the contributions

Figure 7. The $\tilde{X}^2E_{1g}$ state PE spectrum of $C_6H_6^+$ obtained with coupling (red solid line) and without coupling (blue dashed line) to $\tilde{B}^2E_{2g}$ state (a) and (b) present the TDDVR and MCTDH calculated PE spectra, respectively.

Figure 8. (a) presents the experimental $\tilde{D}^2 E_{1u} - \tilde{E}^2 B_{2u}$ PE band of $C_6H_6^+$, whereas (b) and (c) display corresponding theoretical envelope obtained from MCTDH and TDDVR method, respectively. (d) Displays the same band employing the ‘propensity rule’, i.e. $\lambda_{16}^D = \lambda_{17}^D = \lambda_{18}^{DE} = 0$.

for the two individual states, $\tilde{D}^2 E_{1u}$ and $\tilde{E}^2 B_{2u}$, we perform our dynamical calculations separately locating the initial wave packet at $Q = 0$ on those two states. The spectra obtained by individual treatment of $\tilde{D}^2 E_{1u}$ and $\tilde{E}^2 B_{2u}$ states are presented in figure 8c with dot-dash line and dashed line, respectively. The lower energy hump is originated due to the $\tilde{D}^2 E_{1u}$ state, where the $\tilde{E}^2 B_{2u}$ state contributes to the higher energy one. These spectral profiles are convoluted with 1.4 : 1 weight factor and represented in figure 8c by full line. Although the experimental band⁷¹ is more broader than the calculated profile, our results well show the two main peaks and the plateau in between them. It appears that the modes, ν_{16} , ν_{17} , ν_{18} , act both as JT and PJT coupling ones, whereas the ν_{16} and ν_{17} modes show their strong PJT nature and ν_{18} mode effectively acts as JT coupling one. We have also calculated the spectra using ‘propensity rule’,⁵⁵ i.e. $\lambda_{16}^D = \lambda_{17}^D = \lambda_{18}^{DE} = 0$ and presented the same in figure 8d. Along with broad band spectra (figure 8c) with τ value 1.9, the better resolved spectra are calculated by using the larger value of $\tau \sim 19.5$ and displayed the corre-

sponding spectra in figure 9a in comparison with MCTDH one, figure 9b. To elucidate the effect of various modes on the spectra, we calculate the same spectra without PJT modes and display in figure 9c, which shows good agreement with the MCTDH calculated profile (figure 9d). In summary, all the TDDVR calculated results obtained by considering degenerate states in the Hamiltonians show reasonable agreement with the MCTDH calculated spectra.⁵⁹

8. Computational and theoretical aspects of TDDVR approach

All the calculations are performed on a IBM-P-590 cluster with accessible 64 GB RAM and 1.65 GHz clock speed. The server is equipped with 32 Dual-Core (two CPUs in each LPAR) computing nodes (LPARs) with a single symmetric multiprocessing (SMP) configurations. The amount of CPU time needed to perform the dynamics on NO_2^- and $C_6H_6^+$ system using both serial and parallel algorithm are

Figure 9. The figures (a) and (b) present the better resolved theoretical $\tilde{D}^2E_{1u}-\tilde{E}^2B_{2u}$ band obtained with TDDVR and MCTDH method, respectively, whereas (c) and (d) display the same but without PJT modes.

Table 5. A comparison between the computation time of serial and parallelized TDDVR algorithm to study molecular dynamics of NO_2 and C_6H_6^+ .

System	Code	No. of computing nodes	No. of TDDVR basis	Computation time (in hrs)
NO_2	Serial	1	24990	2.6
	Parallel	$6 + 1 = 7$	24990	0.31
C_6H_6^+ ($\tilde{X}^2E_{1g}-\tilde{B}^2E_{2g}$)	Serial	1	14348907	326.5
	Parallel	$36 + 1 = 37$	14348907	31.8
C_6H_6^+ ($\tilde{D}^2E_{1u}-\tilde{E}^2B_{2u}$)	Serial	1	14414517	219.0
	Parallel	$21 + 1 = 22$	14414517	20.5

presented in table 5. The TDDVR approach uses time-dependent DVR basis functions [constructed with GWP multiplied by harmonic oscillator (primitive basis set)], where the calculations of KE matrix elements need to be performed only once for all the time. The movements of the grid-points in the TDDVR are dictated by the so called ‘classical’ mechanics and help to avoid the wastage of many grid-points to represent empty space. In our previous articles,^{33,35,36} we mentioned that TDDVR approach

has the clear scope to scale down the present necessity of CPU time substantially, because it has the possibility to parallelize the major areas of the algorithm. The contributions of different modes on a time-dependent amplitude ($\dot{d}_{i_1, \dots, i_p, l}$) can be evaluated (16) independently, i.e. $\mathbf{Y}_k$ and $\mathbf{Z}_k$ matrices couple grid-points or basis functions of the k th mode only. This feature allows the parallelization of the algorithm, reduces computational time remarkably^{37–39} and pave the possibility to pursue relatively

large dimensional calculations with much less CPU time. The present dynamical calculation has been carried out both serially and parallelly by using $\sim 2 \times 10^7$ number of TDDVR basis functions on each surface for four surface nine mode model Hamiltonian (4). The most time consuming part of TDDVR algorithm is the evaluation of the time-dependent amplitude vector ($\vec{d}_{i_2 \dots i_p, l}$). We need to evaluate the product between wave vector, ($d_{i_2' \dots i_p', l}$) and KE matrix, ($2\bar{Y}_{i_k i_k'} - \bar{Z}_{i_k i_k'}$) (see (16)) to obtain the numerical magnitude of the (16) at each time step. Since the evaluation of this product takes maximum CPU time and the contributions of different modes of each surface (l th) to this product are totally independent from any other calculations, we perform these calculations *parallelly* in different CPUs. As reflected in the table 5 *our parallelized code*^{37–39} *for the TDDVR algorithm reduces the computation time more than an order of magnitude compare to the serial one.*

9. Summary

We have carried out the ‘classical’ trajectory driven quantum dynamics to calculate the broad band as well as better resolved (a) *photodetachment* spectra of NO_2^- , and (b) *PE* spectra of C_6H_6^+ with *degeneracy* among the electronic states (see Hamiltonian (4) and (5)) using our *parallelized* TDDVR approach. The method is flexible enough to handle any form of complexity of the Hamiltonian as well as any relatively large molecular system Hamiltonian. For example, NO_2^- is known as notoriously difficult to produce the photodetachment spectra, whereas the Hamiltonian for C_6H_6^+ consists many DOFs and multiple surfaces. The conically intersecting different states of these systems give rise to a rich structure in their photodetachment/PE spectra which make those systems challenging and interesting representative of the VC mechanism. When sufficient TDDVR basis functions are used for a particular or group of modes, the approach converges to a traditional QM technique where the form of the potential is not a matter of concern. While implementing the TDDVR method on a multi-mode system to investigate its dynamics, the approach can predict the nature of the modes namely deep quantum and quasi-classical and has the scope of handling some of the modes at the quantum limit, others at near classical limit and rest with ‘classical’ mechanics. Since the TDDVR uses time-dependent basis functions/grid-points and does not waste any of them to represent empty space, it

achieves the convergence very fast compared to traditional DVR approaches and thereby, allows one to perform quantum limit calculations even for relatively large dimensional system. In the quantum regime, the dynamics of the centroid of the wave packet obeys the Ehrenfest theorem and facilitates the movement of grid-points, whereas in the classical limit, the centroid of the wave packet and the lone grid-point are the same point and its propagation is dictated by classical dynamics only. The reasonable agreement between theoretically calculated and experimental/QM spectrum shows the applicability of our approach for those relatively large systems where QM description is needed in a restricted region.

Acknowledgement

S A acknowledges the Department of Science and Technology (DST), Government of India for financial support through the project no. SR/S1/PC-13/2008-2011.

References

1. Herzberg G and Longuet-Higgins H C 1963 *Discuss. Faraday Soc* **35** 77
2. Pechukas P 1969 *Phys. Rev.* **181** 174
3. Miller W H and George T F 1972 *J. Chem. Phys.* **56** 5637
4. Davidson E R 1977 *J. Am. Chem. Soc.* **99** 397
5. Blais N C and Truhlar D G 1983 *J. Chem. Phys.* **79** 1334
6. (a) Köppel H, Domcke W and Cederbaum L S 1984 *Adv. Chem. Phys.* **57** 59; (b) Cederbaum L S, Domcke W, Köppel H and Niessen W Von 1977 *Chem. Phys.* **26** 169
7. Tully J C 1990 *J. Chem. Phys.* **93** 1061
8. Gilibert M and Baer M 1994 *J. Phys. Chem.* **98** 12822
9. Sun X and Miller W H 1997 *J. Chem. Phys.* **106** 6346
10. (a) Adhikari S and Billing G D 1998 *Chem. Phys. Lett.* **284** 31; (b) Adhikari S and Billing G D 1998 *Chem. Phys. Lett.* **289** 219; (c) Adhikari S and Billing G D 1999 *Chem. Phys. Lett.* **305** 109
11. Baer M, Lin S H, Alijah A, Adhikari S and Billing G D 2000 *Phys. Rev. A* **62** 32506:1-8
12. Adhikari S, Billing G D, Alijah A, Lin S H and Baer M 2000 *Phys. Rev. A* **62** 032507
13. Adhikari S and Billing G D 2002 *Adv. Chem. Phys.* **124** 143
14. Sarkar B and Adhikari S 2006 *J. Chem. Phys.* **124** 074101
15. Schatz G and Ratner M A 1993 in *Quantum mechanics in chemistry* (Englewood Cliffs: NJ: Prentice Hall)
16. Heller E J 1975 *J. Chem. Phys.* **62** 1544

17. Lee S Y and Heller E J 1982 *J. Chem. Phys.* **76** 3035
18. Meyer H-D 1981 *Chem. Phys.* **61** 365
19. Coalson R D and Karplus M 1982 *Chem. Phys. Lett.* **90** 301
20. Kucar J and Meyer H-D 1989 *J. Chem. Phys.* **90** 5566
21. Möller K B and Henriksen N E 1996 *J. Chem. Phys.* **105** 5037
22. Billing G D 1997 *J. Chem. Phys.* **107** 4286
23. Adhikari S and Billing G D 1999 *Chem. Phys. Lett.* **305** 109
24. Adhikari S and Billing G D 1999 *J. Chem. Phys.* **111** 48
25. Adhikari S and Billing G D 1999 *Chem. Phys. Lett.* **309** 249
26. Adhikari S and Billing G D 2000 *J. Chem. Phys.* **113** 1409
27. Billing G D and Adhikari S 2000 *Chem. Phys. Lett.* **321** 197
28. Barkakaty B and Adhikari S 2003 *J. Chem. Phys.* **118** 5302
29. Puzari P, Deshpande S and Adhikari S 2004 *Chem. Phys.* **300** 305
30. Puzari P and Adhikari S 2004 *Int. J. Quant. Chem.* **98** 434
31. Puzari P, Sarkar B and Adhikari S 2004 *J. Chem. Phys.* **121** 707
32. Puzari P, Sarkar B and Adhikari S 2005 *Int. J. Quant. Chem.* **105** 209
33. Puzari P, Swathi R S, Sarkar B and Adhikari S 2005 *J. Chem. Phys.* **123** 134317
34. Puzari P, Sarkar B and Adhikari S 2006 *Chem. Phys.* **324** 497
35. Puzari P, Sarkar B and Adhikari S 2006 *J. Chem. Phys.* **125** 194316
36. Sardar S, Paul A K, Mondal P, Sarkar B and Adhikari S 2008 *Phys. Chem. Chem. Phys.* **10** 6388
37. Sardar S, Paul A K, Sharma R and Adhikari S 2009 *J. Chem. Phys.* **130** 144302
38. Sardar S, Paul A K and Adhikari S 2009 *Mol. Phys.* **23–24** 2467
39. Sardar S, Paul A K and Adhikari S 2010 *Int. J. Quant. Chem.* (DOI: 10.1002/qua.22578)
40. Tannor D J, Besprozvannaya A and Williams C J 1992 *J. Chem. Phys.* **96** 2998
41. Guo H 1992 *J. Chem. Phys.* **96** 6629
42. (a) Kouri D J, Ma X, Zhu W, Petit B M and Hoffman D K 1992 *J. Phys. Chem.* **96** 9622 (b) Huang Y, Kouri D J, Arnold M, Marchiroll T L and Hoffman D K 1993 *J. Chem. Phys.* **99** 1028
43. Sim E and Makri N 1995 *J. Chem. Phys.* **102** 5616
44. (a) Metz R B, Bradforth S E and Neumark D M 1992 *Adv. Chem. Phys.* **81** 1 (b) Leopold D G, Murray K K, Stevens-Miller A E and Lineberger W C 1985 *J. Chem. Phys.* **83** 4849
45. Weaver A, Metz R B, Bradforth S E and Neumark D M 1989 *J. Chem. Phys.* **90** 2070
46. Ervin K M, Ho J and Lineberger W C 1988 *J. Phys. Chem.* **92** 5405
47. Haller E, Köppel H and Cederbaum L S 1985 *J. Mol. Spec.* **111** 377
48. Ferretti A, Lami A and Villani G 1997 *J. Chem. Phys.* **107** 3498
49. Leitner D M, Köppel H and Cederbaum L S 1996 *J. Chem. Phys.* **104** 434
50. Mahapatra S, Köppel H and Cederbaum L S 1999 *J. Chem. Phys.* **110** 5691
51. Mahapatra S, Köppel H, Cederbaum L S, Stampfuß P, Wenzel W 2000 *Chem. Phys.* **259** 211
52. (a) Hirsch G and Buenker R J 1985 *Can. J. Chem.* **63** 1542; (b) Hirsch G, Buenker R J and Petrongolo 1990 *Mol. Phys.* **70** 835.
53. Köppel H, Cederbaum L S and Domcke W 1988 *J. Chem. Phys.* **89** 2023
54. Köppel H 1993 *Chem. Phys. Lett.* **205** 361
55. Döschner M and Köppel H 1997 *Chem. Phys.* **225** 93
56. Eiding J, Schneider R, Domcke W, Köppel H and Niessen W von 1991 *Chem. Phys. Lett.* **177** 345
57. Döschner M, Köppel H and Szalay P G 2002 *J. Chem. Phys.* **117** 2645
58. Köppel H, Döschner M, Bâldea I and Meyer H-D 2002 *J. Chem. Phys.* **117** 2657
59. Köppel H, Bâldea I and Szalay P G 2003 *Adv. Quan. Chem.* **44** 199
60. Bâldea I and Köppel H 2006 *J. Chem. Phys.* **124** 064101
61. Dirac P A M 1930 *Proc. Cambridge Philos. Soc.* **26** 376
62. Engel V 1992 *Chem. Phys. Lett.* **189** 76
63. Manthe U, Meyer H-D and Cederbaum L S 1992 *J. Chem. Phys.* **97** 9062
64. (a) Gibbs J W 1898 *Nature* **59** 200; (b) Gibbs J W 1899 *Nature* **59** 606
65. Cullum J and Willoughby R 1985 *Lanczos algorithms for large symmetric eigenvalue problems* (Boston: Birkhäuser) vols I and II.
66. Haller E, Köppel H and Cederbaum L S 1985 *J. Mol. Spec.* **111** 377
67. (a) Gillispie G D, Khan A U, Wahl A C, Hosteny R P and Krauss M 1975 *J. Chem. Phys.* **63** 3425; (b) Jackels C F and Davidson E R, 1976 *J. Chem. Phys.* **64** 2908; 1975 *J. Chem. Phys.* **65** 2941
68. (a) Duschinsky F 1937 *Acta Physicochim* **7** 551; (b) Botter R, Dibeler V H, Walker J A and Rosenstock H M 1966 *J. Chem. Phys.* **44** 1271
69. Cederbaum L S and Domcke W 1976 *J. Chem. Phys.* **64** 603
70. Müller H, Köppel H and Cederbaum L S 1993 *New J. Chem.* **17** 7
71. Balzer P, Karlsson L, Wannberg B, Öhrwall G, Holland D M P, MacDonald M A, Hayes M A and von Niessen W 1997 *Chem. Phys.* **224** 95
72. Meyer H-D, Manthe U and Cederbaum L S 1990 *Chem. Phys. Lett.* **165** 73
73. Manthe U, Meyer H-D and Cederbaum L S 1992 *J. Chem. Phys.* **97** 3199
74. Beck M H, Jäckle A, Worth G A and Meyer H-D 2000 *Phys. Rep.* **324** 1