

The time-dependent discrete variable representation (TDDVR) method to the quantum dynamics on ethylene ($C_2H_4^+$)

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Abstract

The molecular dynamics of ethylene radical cation ($C_2H_4^+$) is investigated after excitation from the ground state (X^2B_{2u}) to the first excited electronic state (A^2B_{2g}) by using the time-dependent discrete variable representation (TDDVR) method. The investigation is being carried out with a realistic 3-mode model Hamiltonian of $C_2H_4^+$ molecule. We perform dynamics on the model Hamiltonian consisting most important three vibrational modes to calculate the spectral profile of $C_2H_4^+$ by using TDDVR approach. The TDDVR calculated ultraviolet photoelectron (PE) spectra shows reasonably good agreement with a previous theoretical and the experimental results. It is now established that the TDDVR approach for those molecular systems where quantum mechanical description is needed in a restricted region, is a good compromise between accuracy and speed.

Keywords: Quantum Dynamics, Time Dependent Discrete Variable Representation method, Ethylene

Introduction

The ultrafast relaxation processes after excitation is an important phenomenon in many molecular system due to the fact - non - radiative energy transfer. Such effect become prominent and interesting with the existence of conical intersection(s) between the states and bring a fast pathway for the transfer of population, which are commonly known as non-adiabatic processes[1-4] involved in the dynamics. Such non-adiabatic effects demand rigorous quantum mechanical treatment [5] due to its pure quantum nature. But pure quantum mechanical methods are restricted by computational time with increasing degrees of freedom therefore, our present effort is to establish a quantum-classical method, namely time-dependent discrete variable representation (TDDVR) method.

The formulation of the TDDVR methodology [6-8] has some special characteristics that make it unique dynamical method: (a) TDDVR is appealing from the computational point of view, and (b) it paves the blending of classical and quantum concepts with a new twist. Since GH basis functions are time - dependent and used as the primitive basis to introduce DVR representation, TDDVR has the following advantages: (a) An optimized set of asymmetrically dense grid-points are generated from the Hermite polynomial associated with the eigenfunction of a harmonic oscillator defined around the center of an initial wave packet, GWP [9]. Thus, the required number of grid - points to represent each mode is much less than the case with regularly spaced grid - points; (b) The classical dynamics of the time - dependent parameters of GWP dictates the movement of these unevenly spaced grid - points and thereby, helps to reduce the requirement of the number of grid - points for each mode drastically; (c) Both kinetic - and potential - energy operators appear as local. In each mode, the couplings among the grid - points are through KE matrices, where the potential

energy is diagonal. On the contrary, electronic states are coupled through potential matrix elements defined again at the grid - points. Though the evaluation of KE matrices is needed once for the entire propagation, the diagonal potential energy matrix has to be calculated at each time - step; (d) the contribution of different modes on the time-dependent amplitude of a grid - point of any mode can be found out independently leading to an obvious parallelization of the algorithm. Moreover, since the algorithm does not demand the entire string of amplitudes of the wavefunction at a time to calculate the time - dependence of an amplitude of a grid - point, the required physical memory is negligibly small; (e) The coupled equations for quantum and “classical” dynamics indicate the origin of the stiffness of the differential equations and predict the possibility to eliminate such problems.

In this article, we present the workability of TDDVR method [8,11-13] on a multi - dimensional multi - surface model Hamiltonian of ethylene radical cation ($C_2H_4^+$) to simulate its photoabsorption spectra, where 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. It is important to note that while wave packet moving from one surface to another, the formulation has enough scope to incorporate the details associated with the respective surface through TDDVR basis set as well as time - dependent coefficients; (b) Each TDDVR basis function is obtained by multiplying the corresponding DVR basis with a plane wave, which differs from one surface to another by its parameter; (c) The DVR basis set is constructed by using the eigenfunctions of harmonic oscillator as the primitive one; (d) The plane wave is defined by a classical trajectory and its momentum. When this multi - dimensional multi - surface wavefunction matrix of $C_2H_4^+$ is substituted in the TDSE, we defined 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. With this respect, it is worthy to mention that the width parameters, as defined in the harmonic oscillator eigenfunctions are associated with the on - and off - diagonal elements of the Hamiltonian matrix in the quantum equation of motion, any non - linear “classical” propagation of the width not only increases inaccuracy in the quantum equation of motion but also brings the stiffness in the classical equation of motion. Thus, a fixed width approach either by introducing approximations [6,7] or by using time - independent width parameter¹⁰ is the obvious choice. On the contrary, the “classical” trajectory and its momentum appear with on - diagonal elements of the quantum equation of motion, may affect the convergence but not the final solution of the TDSE. In this version of TDDVR, the formulation is based on time - independent width parameter to bypass all the approximation made earlier and has the scope to derive the variationally optimized classical equation of motion from first principle leading to quantum correction in the classical trajectory or classical feedback to the quantum dynamics in a self consistent manner. The theory can be applied near the classical limit with a few grid - points on a particular mode or in the quantum limit with sufficient grid - points. It is precious to note that TDDVR with one grid - point corresponds to the classical limit known from Newtonian force.

The photo-physics of ethylene cation has brought considerable interest over the past years [14-18] since it provides an insight into the mechanism of molecular dynamics. Historically, the ethylene cation is an example of a important molecular system where the effect of conical intersection on the nuclear dynamics was initially studied [15,16]. This study brought to light that a conical intersection can lead to dramatic failure of the Born - Oppenheimer approximation and even change observables in a qualitative manner. In this work, we have investigated the nuclear dynamics considering the conical intersection of the $C_2H_4^+$ using TDDVR approach where all the three (3) vibrational modes are treated quantum mechanically.

Ethylene molecule is a planar molecule of D_{2h} symmetry, which consists 18 (3N, where N = 6) normal vibrational modes. The electronic ground state configuration of the neutral planar ethylene molecule is: 1a_g²1b_{1u}²2a_g²2b_{1u}²1b_{2u}²3a_g²1b_{3g}²1b_{3u}². The electronic ground and first excited state of the cation has B_{2u} symmetry (X²B_{2u} - state) while first excited state of the cation has B_{2g} symmetry (A²B_{2g}-state). Since the energy separation between the next ionic states is quite large, the higher states can be excluded from our treatment. We have computed the photo-absorption or photoelectron spectra of C₂H₄⁺ with a realistic three (3) mode model Hamiltonian by using our TDDVR approach.

Realistic model Hamiltonian of C₂H₄⁺

The two lowest electronics states of the ethylene radical cation (X²B_{2u} and A²B_{2g}) are populated by photoionization of the neutral ground state. The well known Born-Oppenheimer approximation cannot be used for the description of these two electronic states as they interact via a vibronic coupling mechanism [3]. In the adiabatic representation, the couplings among the states appear through the kinetic energy operator, could diverge at and around the point of conical intersection and thus, the use of diabatic Hamiltonian is a necessity. The detail description of the system dynamics requires a suitable model Hamiltonian that incorporates the symmetry property of the molecule and should reproduce the X²B_{2u} and A²B_{2g} absorption spectra and the fast relaxation. For this reason we are using the well established most realistic model Hamiltonian introduced by Koepfel [15] where the intra and inter state linear coupling terms are involved:

$$\vec{H} = (T_N + V_0) + \begin{bmatrix} a & c \\ c & b \end{bmatrix} \quad (1)$$

where,

$$T_N = -\frac{1}{2} \sum_{i=1}^2 \omega_i \left(\frac{\partial^2}{\partial Q_i^2} \right) - \frac{1}{2} \omega_3 \left(\frac{\partial^2}{\partial Q_3^2} \right),$$

$$V_0 = \frac{1}{2} \sum_{i=1}^2 \omega_i Q_i^2 + \frac{1}{2} \omega_3 Q_3^2,$$

$$a = E_1^0 + \sum_{i=1}^2 \alpha_i^{(1)} Q_i,$$

$$b = E_2^0 + \sum_{i=1}^2 \alpha_i^{(2)} Q_i,$$

$$c = \lambda Q_3.$$

The two terms T_N and V₀ denote the kinetic and potential energy term for the unperturbed harmonic oscillators of all the vibrationally active modes in the system, whereas the 2X2 unit matrix is represented as 1. The quantities E_k⁰ (k = X, A) are the vertical ionization potentials of the corresponding electronic states. The linear intrastate (α_i, i = 1,2) and inter state (λ) coupling constants of the above mentioned Hamiltonian (Eq. 1) are considered to obtain lower resolution PE spectra.

Theoretical background of TDDVR approach

Though the detailed formulations of the different versions of TDDVR approach are presented successively elsewhere [6,8,10] in order to bring the completeness of this article, we briefly demonstrate the relevant equations of the latest one used for current perspective in the simplest but completely generalized way. The basic technical point of TDDVR dynamics is the movement of grid - points (trajectories) by using “classical” equations of motion with time - independent width parameter of the primitive basis set. The form of TDSE in the diabatic representation for the three-mode two-surface model Hamiltonian of ethylene radical cation is given in Eq. (2) as:

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

where

$$\Xi (\{s_k\}, t) \equiv \begin{pmatrix} \psi_1 (\{s_k\}, t) \\ \psi_2 (\{s_k\}, t) \\ \vdots \\ \psi_l (\{s_k\}, t) \\ \vdots \\ \psi_M (\{s_k\}, t) \end{pmatrix} \quad (3)$$

Here, s_k brings the same meaning of Q_k . The l th (the value of l is 2) diabatic wavefunction for many degrees of freedom (p) is expanded in terms of products of TDDVR basis functions for the various k th modes can be expanded as:

$$\Psi_l (\{s_k\}, t) = \sum_{i_1 i_2 \dots i_p} c_{i_1 i_2 \dots i_p, l} (t) \prod_{k=1}^p \psi_{i_k} (s_k, t) \quad (4)$$

$$\psi_{i_k} (s_k, t) = \phi (s_k, t) \sum_{n=0}^{N_k} \xi_n^* (x_{i_k}) \xi_n (x_k) = \sum_{n=0}^{N_k} \xi_n^* (x_{i_k}) \Phi_n (s_k, t)$$

$$\phi (s_k, t) = \pi^{1/4} \exp \left(\frac{i}{\hbar} \left\{ p_{s_c^k} (t) [s_k - s_c^k (t)] \right\} \right) \quad (5)$$

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

$$\xi_n (x_k) = \left(\frac{2 \operatorname{Im} A_k}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{n! 2^n \sqrt{\pi}}} \exp \left(-\frac{x_k^2}{2} \right) H_n (x_k)$$

with

$$x_k = \sqrt{\frac{2 \operatorname{Im} A_k}{\hbar}} (s_k - s_c^k (t)) \quad (6)$$

For any mode k , roots (x_{i_k}) of the Hermite polynomial ($H_N(x_k)$) are fixed points but the positions of the TDDVR grid - points ($s_c^k(t)$) move as a function of s_{ik} ,

$$s_{i_k} (t) = s_c^k (t) + \sqrt{\frac{\hbar}{2 \operatorname{Im} A_k}} x_{i_k} \quad (7)$$

The Gauss-Hermite Basis is an ortho-normal basis and the GWP is orthogonal but not normalized [6,8,10]. When the model Hamiltonian Eq. (1) and the TDDVR representation of wavefunction [Eqs. (3)-(6)] are substituted into the TDSE, the classical path picture appears naturally along with the quantum equation of motion. The compact form of TDDVR matrix equation for quantum motion on the *l*th PES can be written as, where the classical path picture (Eq. 9 and 10) appears naturally along with the quantum counterpart (Eq. 8) [10-12],

$$i\hbar\dot{D}_l(t) = A^{-1/2}H_{ll}'A^{-1/2}D_l + \sum_{l' \neq l} V_{ll'}D_{l'} \quad (8)$$

$$\dot{p}_{s_c^k}(t) = - \left. \frac{dV(\{s_k\})}{ds_k} \right|_{s_k=s_c^k(t)} \quad (9)$$

$$\dot{s}_c^k(t) = \frac{p_{s_c^k}(t)}{\mu} \quad (10)$$

The important characteristics of the TDDVR equation of motion for quantum dynamics have been presented in our previous publications [6, 8] as: (a) The component matrices of the TDDVR Hamiltonian matrix [see Eq. (8)] are time - independent and need to be evaluated once for all; (b) Since the few matrices [10] are diagonal and associated with the “classical” variables, 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 few matrices [11] couple the grid - points and dominate the quantum dynamics, any non - linear “classical” propagation of their associated parameters, {Im A_k}, is not desirable, and hence, a time - independent {Im A_k} is the obvious choice; (d) The contribution of different modes on a time - dependent amplitude (D_l) can be evaluated independently, i.e., Y_k and Z_k matrices couple grid - points or basis functions of the *k* th mode only. This feature allows parallelization of the algorithm reduces computational cost remarkably and paves the possibility to pursue relatively large dimensional calculations. On the other hand, the classical path equations for the *k* th mode are presented in eq. (9) and (10). A rigorous expression of (Q^F_k)(t) is derived by using Dirac - Frenkel variational principle are presented in ref. 10.

Initialization and propagation

Since the multi-mode nuclear dynamics of a molecule is expected to be very efficiently determined [11-13] by using TDDVR approach, our aim is to reproduce the X²B_{2u} and A²B_{2g} photo-absorption spectra of ethylene radical cation with a special interest on intramolecular relaxation and conical intersection expected to play an important role. On the other hand, as the intramolecular relaxation and the effects due to CI are post excitation phenomena, we assume a vertical excitation at the Franck-Condon point (Q=0) just before starting the dynamics so that the initial wavefunction on A²B_{2g} state is same as that for neutral ground state. Thus the starting wavefunction for state A²B_{2g} is a product of Gaussian functions centered on the equilibrium geometry (Q = 0) of the neutral ground state. The details of initialization of the wave packet and its propagation are presented in previous publications [6].

Simulation of photoelectron spectra

The nuclear wavefunction propagated by TDDVR quantum dynamical method is used to calculate the autocorrelation function $C(t)$ and the Fourier transform of $C(t)$ gives X^2B_{2u} and A^2B_{2g} absorption spectra of the ethylene molecule,

$$I(\omega) = \omega \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt \quad (11)$$

$$C(t) = \langle \Psi(t) | \Psi(0) \rangle = \left\langle \Psi^* \left(\frac{t}{2} \right) \middle| \Psi \left(\frac{t}{2} \right) \right\rangle \quad (12)$$

The second form in eq. (12) is more accurate, computationally faster and convenient to implement than the first form. Additionally, the Eq. (12) is valid only when the initial wavefunction is real and the Hamiltonian is symmetric. 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 [6] with appropriate broadening parameter. Though the experimental broadening alone of a spectrum requires a large value of broadening parameter, the calculated spectrum of $C_2H_4^+$ for the three mode model has qualitatively well agreement with the experimental one[14] with broadening parameter = 45 fs.

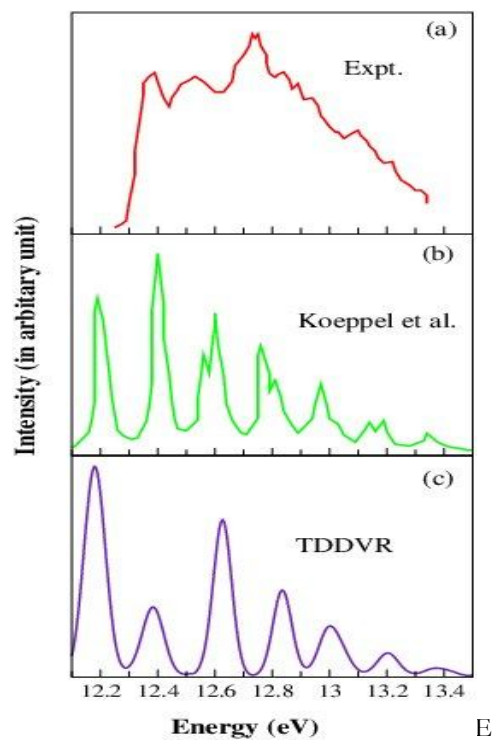


Fig 2: (a) The experimental photoelectron spectra of C_2H_4 ; (b) The spectra calculated [15] by Koeppel with FWHM = 0.02 eV; (c) The spectra calculated with TDDVR method with a damping parameter = 45 fs.

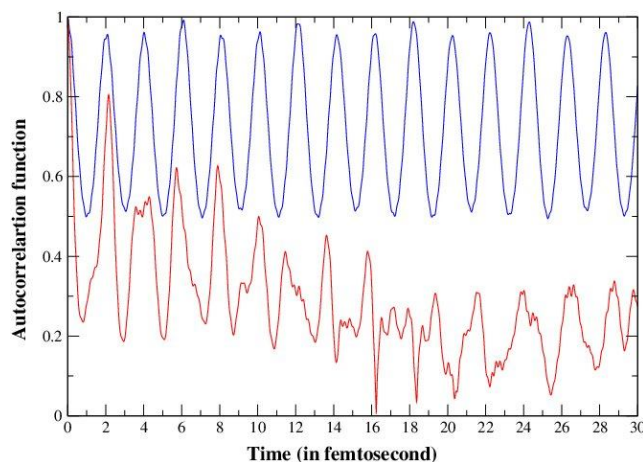


Fig 1: The auto-correlation functions originated from the quantum dynamics of ethylene. The lower (red) and upper (blue) curve indicates the function when the initial wave-function is located on the A and X electronic state, respectively.

In this numerical calculation, the two lowest electronic states of ethylene cation are populated by the excitation, and an autocorrelation function $C(t)$ needs to be obtained for each state. Operationally, we can perform two calculations starting with an initial wave packet $\Psi(0)$ from one of the electronic states (X^2B_{2u} and A^2B_{2g}). The numerical propagation of $\Psi(t)$ is then carried out to obtain the corresponding autocorrelation function and the resulting spectra are calculated according to Eq. (11). Assuming that the ionization of the neutral ground state occurs with the same probability from both (X^2B_{2u} and A^2B_{2g}), we shall add the two computed spectra with equal weights (1:1) to reach the final photo-electron spectra. In this quantum dynamical calculation, the optimum number of TDDVR grid-points used are $N_{\gamma 1}=16$, $N_{\gamma 2} = 16$ and $N_{\gamma 4} = 8$.

Results and discussion

The focus of our investigation is to calculate the auto-correlation function and thereby, to evaluate the photo-electron spectra of ethylene radical cation. We explore the agreement between the calculated spectrum and the experimental one[14]. In our first calculation, the linear coupling Hamiltonian (Eq. 1) is being taken into account by including three vibrational modes of the

two electronic states. Subsequently, the final photo-electron spectra calculation has been performed with those calculated auto-correlation functions.

The TDDVR wavefunction for the three-mode model is propagated up to 400 fs by using 16, 16 and 8 movable grid - points for the tuning mode, γ_1 , γ_2 and the coupling mode (γ_4), respectively. The Eq. (12) implies that the propagation of wavefunction up to 100 fs corresponds to 200 fs in the profile of auto - correlation function. The absolute values of the auto - correlation functions calculated by using the above number of TDDVR basis functions starting with the initial wavefunction at X^2B_{2u} and A^2B_{2g} states are displayed in Fig. 1. Upper panel of Fig. 2 presents the experimentally measured photoabsorption spectrum [14], where the middle panel of Fig. 2 shows the calculated absorption spectra by Koppel et al.[15] (by matrix diagonalization technique). The PE spectra have been computed using the Eq. (11) with linear on- and off-diagonal terms as provided in Table I. The TDDVR calculated spectra shows excellent agreement with the experimental one. The individual electronic state (X^2B_{2u} and A^2B_{2g}) spectra of both states are presented in the two panels of Fig. 3. The upper and lower panels of the Fig. 4 display the diabatic state population as a function of time again starting with the initial wavefunction at A^2B_{2g} and X^2B_{2u} state, respectively. It is interesting to observe that the population profile in Fig. 4 corresponds very well with the spectrum as shown in the lower panel of Fig. 2. The same calculation has been performed with smaller number of grid points, but the calculated spectra differ little only at longer time. Since the loss of coherence throughout the whole propagation is small, and in principle, the TDDVR method with sufficient grid - points can reproduce the exact quantum mechanical results, we wish to perform TDDVR calculations with the smaller set of basis functions so that, the results are close enough to the exact quantum one and more number of grid-points could be included explicitly in the dynamical process. The upper and lower panels of the Fig. 4 demonstrate the change of system population density of the 3 - mode model as function of time, when the dynamics is performed starting the initial wavefunction at X^2B_{2u} and A^2B_{2g} state, respectively. The peaks/spikes in these figures clearly indicate the role of conical intersection in the dynamics.

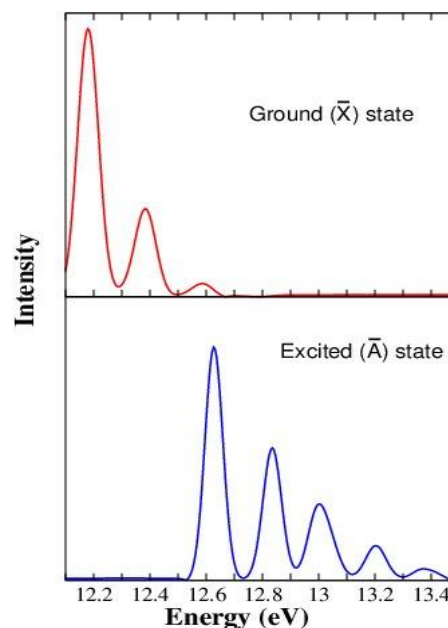


Figure 3: The simulated PE spectra by TDDVR method for ground (\bar{X}) state (upper panel) and excited (\bar{A}) state (lower panel) with a damping parameter = 45 fs.

Computational and theoretical aspects of the TDDVR approach

The TDDVR approach uses time - dependent DVR basis functions (constructed with GWP multiplied by harmonic oscillator (primitive basis set)), the calculations of potential energy matrix elements need to be performed only once for all the time. The movements of the grid - points in the TDDVR are dictated by so called “classical” mechanics and help to avoid the wastage of many grid - points to represent empty space. At this junction, we also wish to mention that the TDDVR approach has the clear scope to scale down the physical memory and CPU time substantially since it can be parallelized [11-13] the major areas of the algorithm. The contribution of different modes on a time - dependent amplitude (D) can be evaluated [Eq. (8)] independently, i.e., Y_k and Z_k matrices couple grid - points or basis functions of the k th mode only. This feature will allow parallelization of the algorithm, reduce computational cost remarkably and pave the possibility to pursue relatively large dimensional calculations. Moreover, we remind that the expansion of wavefunction in terms of TDDVR basis set can be such that one may also introduce the idea of mode combination either based on physical and/or symmetry consideration to reduce the computational cost. Of course, the correlation among the modes is a necessity to increase accuracy and its implementation in our

TDDVR approach is definitely possible. At present, we are parallelizing the code and introducing the scope to incorporate the symmetry of the Hamiltonian. We have done all the calculations on a normal PC with 4 GB RAM and 3.1 GHz clock speed. The amount of physical memory used and CPU time needed to perform the dynamics of three - mode model are 100 Mbytes and 10 minutes, respectively. The dynamics has been carried out by using 105 number of TDDVR grid - points on each surface.

Summary

A quantum dynamical study has been performed on ethylene radical cation by using the TDDVR approach considering a three - mode realistic model Hamiltonian to calculate its photoabsorption spectrum due to the excitation from neutral ground state to X^2B_{2u} and A^2B_{2g} , respectively. The method is enough flexible to handle any form of complexity of the Hamiltonian expressed in Cartesian coordinates. When sufficient TDDVR grid - points/basis functions are used for a particular or group of modes, the approach converges to a traditional quantum mechanical 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

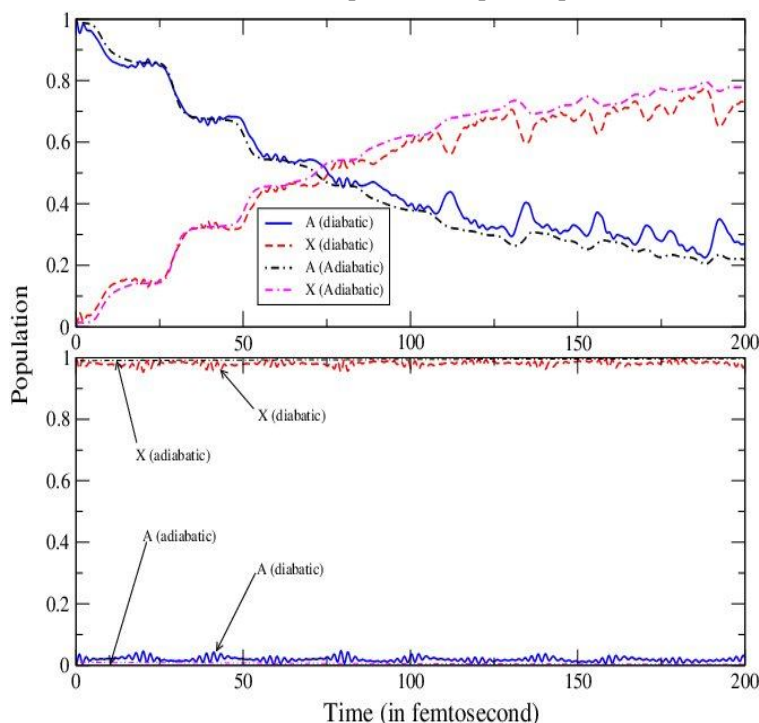


Figure 4: The population dynamics of the $C_2H_4^+$ when initial wave function is located on (i) A (upper panel) and (ii) X (lower panel) state.

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. In case of present Hamiltonian, the coupling and the tuning modes are being described with sufficient TDDVR basis to treat them in the quantum limit. The reasonable agreement between theoretically calculated and experimental/quantum mechanical spectrum shows the applicability of our approach for those large systems where quantum mechanical description is needed in a restricted region.

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