Classical description of ultrafast internal conversion processes.  
The benzene cation  

Gerhard Stock  
Institute of Physical and Theoretical Chemistry, Technical University of Munich, D-85748 Garching, Germany  
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Abstract

Based on the classical electron analog model due to Meyer and Miller, a classical approach to the microscopic modelling of ultrafast internal conversion processes in polyatomic molecules is outlined. Adopting a recently proposed multimode model of the \( \tilde{X}^2E_{1g}, \tilde{B}^2E_{2u} \) and \( \tilde{C}^2A_{2u} \) electronic states of the benzene cation (Köppel), we present computational studies on the \( \tilde{C} \rightarrow \tilde{B} \rightarrow \tilde{X} \) electronic relaxation process in this molecular system. The classical model is shown to be in semi-quantitative agreement with quantum mechanical five-mode reference calculations, reproducing nicely transient features as well as long-time limits of the diabatic electronic population probabilities. Including the remaining important vibrational modes and vibronic interactions of the benzene cation into the model description, the classical simulations predict internal conversion decay times of \( T_{CE} \approx 6 \) fs for the \( \tilde{C} \rightarrow \tilde{B} \) and \( T_{XB} \approx 42 \) fs for the \( \tilde{B} \rightarrow \tilde{X} \) transition.

1. Introduction

Internal conversion (IC) processes of molecular systems have received a great deal of attention over the past few decades [1–14]. The existence of rapid radiationless electronic relaxation dynamics can be inferred, e.g. from the absence of detectable fluorescence in polyatomic cations [6] and higher-lying excited electronic states of polyatomic molecules [7,8]. The theoretical description of IC processes is closely related to a number of longstanding research topics, including intramolecular vibrational relaxation, the question of irreversibility in a finite-dimensional quantum system, and the question of whether the relaxation process under consideration is more appropriately characterized by a statistical or by a dynamical theory [1–5,10].

The majority of theoretical work on IC has employed the fruitful 'Golden Rule' description to calculate electronic decay rates [1–5]. Dealing however with ultrafast IC processes occurring on timescales of the order of a few hundreds of femtoseconds, it appears to be questionable whether it is appropriate to treat the corresponding strong intramolecular interactions by a perturbative approach. Employing exact time-dependent quantum calculations with up to five non-separable vibrational degrees of freedom, Köppel, Domcke, Cederbaum and co-workers have investigated the ultrafast electronic and vibrational relaxation dynamics of a variety of model systems including \( \text{C}_2\text{H}_2^+ \) [9–11], pyrazine [10,11] and \( \text{C}_6\text{H}_5^+ \) [12–14]. Quite recently, Köppel presented interesting quantum calculations of the ultrafast IC in the benzene cation (Bz+) [14]. Including five vibrational modes and accounting for the vibronic interactions between the \( \tilde{X}^2E_{1g}, \tilde{B}^2E_{2u} \) and \( \tilde{C}^2A_{2u} \) electronic states of Bz+, he showed that the (initially excited) \( \tilde{C} \) state decays irreversibly into the \( \tilde{X} \) state within \( \approx 250 \) fs.

In this Letter, we use the Bz+ model of Köppel to demonstrate the capacity and accuracy of the classical
electron analog (CEA) approach [15] for the description of ultrafast IC processes. There is a number of theoretical concepts that incorporate electronic degrees of freedom into a classical theory, such as 'rigorous' semi-classical methods [16-18], various versions of the surface hopping model of Tully and Preston [19-24], and a variety of classical path models (i.e. classical nuclear motion coupled to time-dependent electronic motion) [15,25,26]. The classical electron analog model due to Meyer and Miller [15] is a classical path method that treats both electronic and nuclear degrees of freedom on an equal dynamical footing. The model has been successfully applied to a variety of model problems, including the evaluation of non-adiabatic collision cross sections [27,28], the photodissociation of non-adiabatically coupled electronic states [29,30], and the calculation of non-Born-Oppenheimer dynamics of conical intersections [31-34].

We first demonstrate that the CEA model reproduces the quantum-mechanical results of Köppel surprisingly accurately. Long-time limits as well as short-time coherent beatings of the electronic population probabilities are reproduced semi-quantitatively. Including the remaining important vibrational degrees of freedom and taking into account the degeneracy of the X and B electronic states and the (pseudo-)Jahn-Teller active modes, we perform computational studies on the electronic relaxation of Bz⁺. The classical simulations predict IC decay times of T_{BoX} \approx 6 fs for the C→B and T_{XBo} \approx 42 fs for the B→X transition. According to these predictions, the IC process in Bz⁺ is one of the fastest intramolecular relaxation processes known to date.

2. Quantum-mechanical model

In a diabatic electronic representation [35], the Hamiltonian for the lowest three electronic states of Bz⁺ can be written as

$$H = \sum |\phi_k\rangle \langle T + V_k| + \sum |\phi_k\rangle V_{kk'} \langle \phi_{k'}|,$$

where \(k = X, X, B, \bar{B}, \bar{C}\), i.e. the second excited electronic state (\(\bar{C}^2A_{2u}\)) is represented by |\(\phi_{\bar{C}}\rangle\), while |\(\phi_{X}\rangle\), |\(\phi_{X}\rangle\), and |\(\phi_{B}\rangle\), |\(\phi_{\bar{B}}\rangle\) denote the degenerate electronic ground (\(\bar{X}^2E_{2u}\)) and first excited (\(\bar{B}^2E_{2u}\)) electronic state, respectively. As is common practice in vibronic coupling theory [9,36], we approximate the diabatic potential matrix elements \(V_{kk'}\) and the diabatic coupling \(V_{kk'}\) by a Taylor expansion in the (dimensionless) normal coordinates of the electronic ground state of neutral benzene. Adopting matrix notation, the electronic potential matrix reads [14]

$$V = U_0 + \sum \left[ \begin{array}{cccc}
E_X + \sum_{i=1}^{9} \kappa_i^{(X)} Q_i & \sum_{i=6}^{9} l_i^{(X)} \rho_i e^{-i\theta} & -\sum_{i=4}^{5} \kappa_i Q_i & 0 \\
\sum_{i=6}^{9} l_i^{(X)} \rho_i e^{i\theta} & E_X + \sum_{i=1}^{2} \kappa_i^{(X)} Q_i & 0 & \sum_{i=4}^{5} \kappa_i Q_i \\
0 & \sum_{i=6}^{9} l_i^{(B)} \rho_i e^{-i\theta} & E_B + \sum_{i=1}^{2} \kappa_i^{(B)} Q_i & \sum_{i=16}^{17} \lambda_i r_i e^{i\theta} \\
o & \sum_{i=6}^{9} l_i^{(B)} \rho_i e^{i\theta} & E_B + \sum_{i=1}^{2} \kappa_i^{(B)} Q_i & \sum_{i=16}^{17} \lambda_i r_i e^{-i\theta}
\end{array} \right].$$

Here, \(T + U_0\) represents the harmonic oscillator Hamiltonian of the electronic ground state of neutral benzene, \(E_k\) is the vertical transition energy of the diabatic state |\(\phi_k\rangle\>, and \(\kappa_i^{(k)}\) \((i = 1, 2)\) denotes the gradient of the excitation energy with respect to the totally symmetric coordinates \(Q_i\). The model Hamiltonian (1) features three different kinds of vibronic interactions: the Jahn–Teller coupling owing to the degeneracy of the \(\bar{X}\) and \(\bar{B}\)
states through the modes $\nu_6-\nu_9$ (Wilson numbering), the coupling of the $C$ and $B$ states by the pseudo-Jahn–Teller active modes $\nu_6$ and $\nu_7$, and the coupling of the $B$ and $X$ states by the modes $\nu_4$ and $\nu_5$. As has been discussed in detail elsewhere [9,12–14], each of the vibronic interactions leads to a multidimensional conical intersection of the corresponding potential energy surfaces. All parameters of the model Hamiltonians (1) and (2) are taken from Ref. [14]. For a further discussion of the Hamiltonian (1) see Refs. [13,14].

To be able to perform quantum-mechanical wave-packet propagations, the Hamiltonian is simplified by neglecting the presumably weaker coupled modes $\nu_2, \nu_3, \nu_7, \nu_9$ and $\nu_{16}$. Ignoring furthermore the degeneracy of the remaining vibrational modes $\nu_6, \nu_8, \nu_7$ and the $X$ and $B$ electronic states, the model system (1) reduces to the 3-state 5-mode Hamiltonian [14]

$$
H = (T + U_0) 1 +
$$

Using the model Hamiltonian (2), Köppel performed large-scale dynamical quantum calculations by solving numerically exactly the time-dependent Schrödinger equation. As initial state it has been assumed that the system is in the vibrational ground state of neutral benzene shifted up vertically to the $C$ potential energy surface, corresponding to ionization from the electronic and vibrational ground state of neutral benzene.

3. Classical model

The CEA model is based on the observation that for a finite dimensional quantum mechanical system a formally exact classical analog can be defined by representing the $N_d$ quantum mechanical states $\{ |\phi_k \rangle \}$ by $N_{cl}$ pairs of classical action-angle variables $\{ n_k, q_k \}$ [15]. Within this theoretical framework the classical Hamiltonian function $H$ corresponding to the quantum mechanical Hamiltonian operator (1) is given by ($\hbar = 1$)

$$
H(p, x, n, q) = \frac{p^2}{2\mu} + \sum_k n_k V_k(x) + \sum_{k \neq k'} \sqrt{(n_k + \frac{1}{2})(n_{k'} + \frac{1}{2})} \exp[i(q_k - q_{k'})] V_{kk'}(x). \tag{3}
$$

The CEA Hamiltonian function depends parametrically (through the diabatic potential matrix elements $V_k(x), V_{kk'}(x)$) on the nuclear coordinates $x$, where $x$ denotes collectively all vibrational modes of the system. To obtain a dynamically consistent model within the framework of classical S-matrix theory [37], Langer-type modifications have been employed in the off-diagonal terms [15]. The time evolution of both heavy-particle degrees of freedom ($p, x$) and electronic degrees of freedom ($n, q$) are then described consistently by Hamilton’s equations

$$
\begin{align}
\dot{p}_i(t) &= -\frac{\partial H}{\partial x_i}, \\
\dot{x}_i(t) &= \frac{\partial H}{\partial p_i} \quad (i = 1, ..., N_{mod}), \\
\dot{n}_k(t) &= -\frac{\partial H}{\partial q_k}, \\
\dot{q}_k(t) &= \frac{\partial H}{\partial n_k} \quad (k = 1, ..., N_{el}).
\end{align} \tag{4a}
$$

Note that, although the electronic degrees of freedom are incorporated into the classical theory in a ‘semiclassical’ manner [15], the computational effort truly scales only linearly with the number of both electronic and nuclear degrees of freedom.

To avoid the cumbersome complex potential matrix elements in (1) comprising the degenerate Jahn–Teller modes ($\nu_6-\nu_9$) and pseudo-Jahn–Teller modes ($\nu_{16}, \nu_{17}$), we employ real Cartesian-like coordinates instead of
the more usual complex polar coordinates [9]. Choosing action-angle initial conditions for both electronic and nuclear degrees of freedom [31], the equations of motion (4) are integrated using a standard Runge-Kutta-Merson routine. For all classical simulations the number of trajectories has been chosen as $N_{\text{traj}} = 1000$, although the essential structures may already be recognized with less than hundred trajectories.

4. Time-dependent electronic observables

In the discussion of radiationless processes (as well as of any reactive process) the main quantity of interest is represented by the rate of the reaction. Pursuing time-dependent wavepacket propagations on coupled electronic potential-energy surfaces, one directly evaluates the time-dependent population probabilities $P_k(t)$ of the $k$th electronic state. In the case that $P_k(t)$ may be fitted in some sensible way to an exponential function, the rate of the IC process is then given by $P_k/P_k$. The time-dependent population probabilities of the diabatic electronic state $|\varphi_k\rangle$ is defined as the expectation value of the diabatic projector $P^d_k$

$$ P^d_k(t) = \langle \Psi(t) | P^d_k | \Psi(t) \rangle , $$

$$ P^d_k = |\varphi_k\rangle \langle \varphi_k| , $$

where $|\Psi(t)\rangle = e^{-iHt} |\Psi(0)\rangle$ is the intramolecular wavefunction. Transitions between diabatic electronic states are important for the interpretation of spectroscopic data [9,12], as in the vicinity of a conical intersection the electronic dipole transition operator is only smooth in the diabatic representation [35].

Regarding IC as a chemical reaction, however, one would be interested in the population probabilities of the adiabatic electronic states. In a diabatic representation, the projector onto the $k$th adiabatic electronic state is defined by

$$ P^a_k = S(x) p^d_k S^*(x) , $$

where

$$ S(x) = \sum_{k,k'} |\varphi_k\rangle S_{kk'}(x) \langle \varphi_{k'}| $$

denotes the unitary transformation between the diabatic and adiabatic wavefunctions [9,11]. Quantum mechanically, the evaluation of the adiabatic population probabilities via Eq. (7) is a rather time-consuming task [11], requiring about as much computational effort as the entire wave-packet propagation in the diabatic representation.

In the CEA model the diabatic electronic population dynamics is described by the classical action variables $n_k(t)$ which, by virtue of the Langer-like modifications, can take on continuous values from $-\frac{1}{2}$ to $\frac{1}{2}(N_e+1)$. To make the correspondence to discrete electronic states (i.e. $n_k=0$ or 1) we invoke a histogram method [38] of assigning the system to the diabatic electronic state with the largest $n_k(t)$, i.e.

$$ P^a_k(t) = \frac{1}{N_{\text{traj}}} \sum_{i=1}^{N_{\text{traj}}} \chi(n_k^i(t)) , $$

$$ \chi(n_k) = 1 \quad \text{if } n_k > n_{k'} , $$

$$ \chi(n_k) = 0 \quad \text{otherwise} . $$

If the electronic state under consideration is degenerate (say, in case of the $\tilde{X}$ state), the total population of the $\tilde{X}$ electronic state is evaluated, i.e. the sum of the corresponding action variables is histogrammed $\chi(n_{\tilde{X}}(t) + n_{\tilde{X}}(t))$ [39].

The calculation of the time-dependent adiabatic population probabilities is fairly easy in the CEA formalism,
because the classical evaluation of the adiabatic projections (7) requires only manipulations of \( N_e \times N_e \) matrices, whereas quantum mechanics requires manipulations in the full electronic-vibrational product space. For an electronic two-state problem the adiabatic population probability can be evaluated analytically \([32]\), for \( N_e > 2 \) the transformation matrix \( S(x) \) is readily obtained by diagonalizing the diabatic potential matrix. Defining the electronic matrix elements of the adiabatic projector as

\[
p^{(k)}_{\text{ad}}(x) = \langle \phi_i | S(x) | \phi_j \rangle = \langle \phi_i | S(x) S^\dagger(x) | \phi_j \rangle ,
\]

the population probability of the \( k \)th adiabatic state is given by

\[
P^{(k)}_{\text{ad}}(t) \approx \sum_{i,j} \langle \nadm^{(k)}(t) \rangle ,
\]

where

\[
\nadm^{(k)}(t) = \sum_i \langle \bar{\phi}_i | p^{(k)}_{\text{d}} | \bar{\phi}_j \rangle + \sum_{i,j} \sqrt{(n_i + \frac{1}{2})(n_j + \frac{1}{2})} \exp[i(q_i - q_j)] p^{(k)}_{\text{d}}.
\]

Eq. (13) is an example of the general feature of the CEA model that any quantum-mechanical operator (here \( p^{(k)}_{\text{d}} \)) is represented by a classical function (here \( \nadm^{(k)} \)) through its diabatic electronic matrix elements (here \( p^{(k)}_{\text{d}} \)) and the prescription equation (13) \([15]\). Note that the classical evaluation of \( \nadm^{(k)}(t) \) is invariant to a sign change of an eigenvector in the unitary transformation \( S(x) \). Unlike a quantum calculation, there are therefore no problems with discontinuities in the transformation \( S(x) \), which are a consequence of the geometric phase acquired by the wavefunction in the vicinity of a conical intersection \([40]\). This also implies that the corresponding quantum information is lost in the classical model.

5. Computational results and discussion

To obtain an impression as to what extent the classical model is capable of mimicking quantum dynamics on coupled potential energy surfaces, Figs. 1a and 1b compare the quantum \([14]\) and classical calculations of the diabatic population probability of the 5-mode 3-state model (Eq. (2)) of \( \text{Bz}^+ \). The quantum calculation exhibits an oscillatory population decay of the initially excited \( \text{C} \) electronic state, which is reflected in a rapid rise and similar beatings of the \( \text{X} \) state population. After a somewhat delayed onset, the population of the \( \text{B} \) electronic state exhibits a non-oscillatory rise and dominates over both the \( \text{C} \) and \( \text{B} \) electronic states after \( \approx 120 \text{ fs} \). The classical calculation, shown in Fig. 1b, is seen to reproduce the features of the quantum reference, e.g. transient beatings and long-time limits, fairly well. Except for the amplitude of the quantum beats and the classically somewhat exaggerated \( \text{B} \rightarrow \text{X} \) decay, the agreement of quantum and classical calculations is almost quantitative. Considering the simplicity of the classical model (on a standard workstation the quantum calculations took 2 CPU days compared to 20 CPU min for the classical calculation), the accuracy of the classical method is surprising.

Having checked the reliability of the CEA description for the 5-mode 3-state model of \( \text{Bz}^+ \), we now want to take advantage of the possibilities of the classical method and study the ultrafast electronic relaxation of \( \text{Bz}^+ \) in some more detail. Let us first consider the \( \text{C} \rightarrow \text{B} \rightarrow \text{X} \) IC process in an adiabatic picture, and look at the adiabatic population probabilities displayed in Fig. 1c. As has been found also for two-state conical intersection problems \([11]\), the adiabatic population of the initially excited \( \text{C} \) electronic state decays within less than a vibrational period almost completely into the lower-lying \( \text{B} \) state. The \( \text{C} \rightarrow \text{B} \) adiabatic decay is thus faster than the corresponding diabatic decay, whereas the slower rise of the \( \text{X} \) state population is almost identical in both the diabatic and the adiabatic picture. For larger times (i.e. \( t > 400 \text{ fs} \)), the values of the adiabatic populations remain constant, i.e. within the 5-mode 3-state model the excited-state populations do not decay completely into the electronic ground state of the system.
Fig. 1. Time-dependent population probabilities of the (---) C, (•••) B and (---) X electronic states of the 5-mode 3-state model of the benzene cation. Panel (a) shows the quantum [14] and panel (b) the classical calculation of the diabatic population probabilities. The population probabilities of the adiabatic electronic states obtained in the classical model are shown in panel (c).

The most important feature of the CEA model compared to a quantum method is that it is an easy matter to take into account many electronic and vibrational degrees of freedom. As a demonstration of the capacity of the classical method, we investigate the relaxation dynamics of the more realistic model system (Eq. (1)) for Bz⁺, where the remaining vibrational modes ν₂, ν₅, ν₇, ν₉ and ν₁₆ are included and the degeneracy of the (pseudo-)Jahn–Teller modes and the X and B electronic states are explicitly taken into account. Fig. 2 shows the diabatic (a) and adiabatic (b) population probabilities of the resulting 16-mode 5-state model of Bz⁺. The plot is reminiscent of a textbook example for consecutive chemical reaction kinetics, \( C \rightarrow B \rightarrow X \), where the \( B \rightarrow X \) decay represents the rate-determining step. Although the adiabatic C population decays somewhat faster than the corresponding diabatic one, both diabatic and adiabatic population probabilities are seen to decay/rise in a similar way without oscillatory transients. Within less than 100 fs the initially excited C electronic state is completely decayed into the electronic ground state of the system, yielding IC decay times of \( T_{XC} \approx 6 \) fs for the \( C \rightarrow B \) and \( T_{XB} \approx 42 \) fs for the \( B \rightarrow X \) transition.

Note that the IC process described by the 16-mode 5-state model is considerably faster (roughly by a factor of three) than the IC process in the 5-mode 3-state model of Bz⁺. A detailed computational study of the intramolecular vibrational relaxation dynamics of the two models of Bz⁺ shows that the faster decay is mainly a consequence of the effective energy redistribution in the additional Jahn–Teller active modes ν₁ and ν₉ [39]. The simulations reveal that the ultrafast electronic relaxation is intimately related to multimode vibrational relaxation on the lower-lying potential energy surfaces [10,39].

Finally, it should be pointed out that Fig. 2 demonstrates an irreversible decay of a finite-dimensional bound-state system. In other words, the level density corresponding to 16 vibrational degrees of freedom and the intra-
molecular couplings contained in the model Hamiltonian (1) appear to be sufficient to simulate dissipative dynamics of a closed system.

6. Concluding remarks

Adopting Köppel's 5-mode model of the first three electronic states of Bz+, we have demonstrated the accuracy of the capacity of the CEA model for the description of ultrafast IC processes. The classical model was shown to reproduce nicely transient features as well as long-time limits of the diabatic population probabilities of the quantum-mechanical reference calculations. Along with preceding investigations on the relaxation dynamics of multimode two-state systems [31–34], the computational studies confirm that the CEA model appears to be especially suited to the dynamical description of these multi-dimensional strongly-coupled molecular systems.

To the best of our knowledge this is the first computational application of the CEA model for more than two interacting electronic states. Although the generalization to \( N_{ee} > 2 \) is straightforward within the CEA formalism, the central 'mean path' approximation and the semiclassical implications (i.e. the Langer-like modifications) of the model require, in practice, careful computational studies on the model system under consideration [39].

Including the remaining important vibrational modes and vibronic interactions of Bz+, the classical simulations predict a truly ultrafast \( \tilde{\mathbf{C}} \to \tilde{\mathbf{B}} \to \tilde{\mathbf{X}} \) IC process which is completed within \( \approx 100 \) fs. This conclusion is fully consistent with the experimental lower limit for the non-radiative decay rate of Bz+, \( \kappa_{nr} > 10^{12} \) s\(^{-1}\), corresponding to an excited electronic state lifetime shorter than 200 fs [41].

Besides treating many intramolecular degrees of freedom, it is clear that the CEA method also allows an investigation of electronic relaxation in the presence of many intermolecular degrees of freedom, i.e. in solution. Electronic relaxation of a chromophore in solution, usually referred to as electron transfer, is intimately related to IC in a complex molecular system. CEA simulations of electron transfer on coupled electronic potential energy surfaces would represent an intriguing approach for gaining a more microscopic understanding of these processes.
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