

Inclusion of Machine Learning Kernel Ridge Regression Potential Energy Surfaces in On-the-Fly Nonadiabatic Molecular Dynamics Simulation

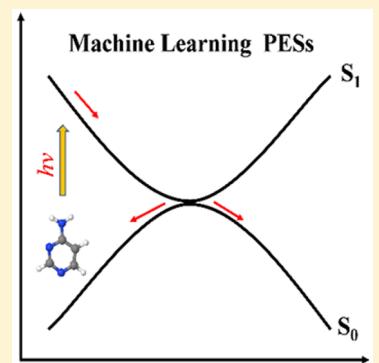
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Supporting Information

ABSTRACT: We discuss a theoretical approach that employs machine learning potential energy surfaces (ML-PESs) in the nonadiabatic dynamics simulation of polyatomic systems by taking 6-aminopyrimidine as a typical example. The Zhu–Nakamura theory is employed in the surface hopping dynamics, which does not require the calculation of the nonadiabatic coupling vectors. The kernel ridge regression is used in the construction of the adiabatic PESs. In the nonadiabatic dynamics simulation, we use ML-PESs for most geometries and switch back to the electronic structure calculations for a few geometries either near the S_1/S_0 conical intersections or in the out-of-confidence regions. The dynamics results based on ML-PESs are consistent with those based on CASSCF PESs. The ML-PESs are further used to achieve the highly efficient massive dynamics simulations with a large number of trajectories. This work displays the powerful role of ML methods in the nonadiabatic dynamics simulation of polyatomic systems.



Nonadiabatic transition plays an important role^{1,2} in plenty of photochemical and photophysical processes, such as the photostability of biological polyatomic systems,^{3–5} the photoisomerization of organic conjugated alkenes and their derivatives,^{6,7} and the photoreactions of transition metal complexes.^{8,9} In the vicinity of conical intersections (CIs), the strong interstate coupling drives ultrafast nonadiabatic processes, in which the Born–Oppenheimer approximation breaks down.^{1,2} Various nonadiabatic dynamics methods have been developed, including quantum dynamics^{1,2,10–12} and mixed-quantum-classical or semiclassical dynamics.^{13–21}

The trajectory surface hopping (TSH) method^{22–25} is a widely used mixed quantum–classical method for the treatment of nonadiabatic dynamics. Different methods have been proposed to define the hopping probability in the TSH dynamics. One approach assumes that the hopping probability is relevant to the electronic evolution governed by time-dependent quantum mechanics. One widely used approach that belongs to this theoretical framework is the fewest-switches algorithm proposed by Tully.²² Alternatively, it is also possible to use a predefined probability, for instance, based on the Landau–Zener formulism,²⁶ in the TSH calculations. Along this line, Zhu and Nakamura developed the Zhu–Nakamura method to calculate the nonadiabatic transition probability.^{27,28} Later, Zhu and coworkers proposed the simplified Zhu–Nakamura formulism to calculate the hopping probability, which does not require the calculation of nonadiabatic coupling vectors (NACVs) in the TSH simulation.^{29–31} Although it is a rather simplified method, this approach shows promising results

with respect to those obtained from Tully's surface-hopping dynamics method.³¹

Independent of the dynamical method chosen to treat nonadiabatic processes, one key step is to obtain the potential energy surfaces (PESs) and their couplings. It is possible to build the PESs before the dynamics run.³² This so-called “PES-fitting” method generally assumes the particular functions of the PESs and then fits the relevant parameters on the basis of experimental data or electronic structure calculations. A large amount of electronic structure calculations over an extensive high-dimensional grid should be performed to build the database for fitting, which becomes a difficult task with an increasing system size. It is also not trivial to define the suitable active coordinates in the PES construction for large systems.

Alternatively, when mixed quantum–classical dynamics is considered, it is possible to perform the electronic structure calculations in an on-the-fly manner. During the past decade, great efforts were made to combine the direct dynamics with mixed quantum–classical dynamics for the atomic treatment of the nonadiabatic dynamics of complex systems with all degrees of freedom.^{32–41} On-the-fly TSH calculations may suffer from an enormous computational cost because the electronic structure calculations are performed at each time step of nuclear motion. This computational cost prevents the

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simulation of a large number of trajectories, particularly for complex systems.

Recently, the machine learning (ML) approach has been widely used in various fields,⁴⁵ such as brain–computer interfaces, pattern recognition, recommender systems, and robotics. The supervised ML methods have been applied very successfully in many fields of chemistry,^{43,44} including the structure–property relation,^{45–48} the construction of PESs,^{49–63} and the excitonic dynamics.⁶⁴ In the study of ground-state dynamics, various ML approaches have been proposed to construct the PESs, including kernel ridge regression (KRR),^{65–67} artificial neural network (ANN),^{43,49–51,54,56–58,61–63,68–75} and Gaussian process models.⁷⁶ Although ML-PESs have started to become important in ground-state dynamics simulations, the employment of ML-PESs in the excited-state nonadiabatic dynamics simulation is still limited.^{61,64,73,77}

In recent years, some efforts have been made to construct the diabatic PESs and the interstate couplings of middle-sized molecules.^{61,64,73,77–81} These efforts either assume analytical PES functions in the fitting procedure or employ ML approaches to build the PES functions. This approach provides the possibility to simulate the full-dimensional nonadiabatic dynamics of complex systems with accuracy and efficiency. Most of these studies have tried to fit the diabatic PESs and couplings because the physical properties become smooth in a diabatic representation. However, the construction of the diabatic model is extremely challenging in complex systems. In addition, it is not easy to define suitable coordinates in the fitting procedure.

In this work, we attempted to combine the ML-PESs and the nonadiabatic dynamics simulation. We utilized a rather simple approach to perform the TSH simulation on the basis of the Zhu–Nakamura algorithm.^{29–31} As mentioned in a previous study,³¹ the Zhu–Nakamura method can provide a reasonable description of the nonadiabatic dynamics of polyatomic systems. The further approximation of the Zhu–Nakamura algorithm in the TSH method does not need NACVs.^{29–31} We chose 6-aminopyrimidine (6AP)⁸² as a typical system to explain our approach. After the construction of the molecular descriptor via the Coulomb matrix (CM),^{46,47,64} we attempted to employ the KRR^{65–67} approach to build the adiabatic PESs. After we carefully controlled the sampling and fitting procedure, the fitted PESs performed very well along the pathway. In the nonadiabatic dynamics simulation, we mainly used the resulting ML-PESs for most structures. To avoid possible ML-PES fitting errors relevant to the double-cone topology of the PESs, we switched back to the electronic structure calculations for only a few geometries when the trajectory enters areas in the vicinity of the CI seam. This approach provides an excellent balance between computational cost and accuracy. As a complementary study, we also ran two sets of on-the-fly TSH simulations based on both Zhu–Nakamura’s and Tully’s methods to check the accuracy of the former approach.

As a pyrimidine heterocycle and a reduced model of adenine, 6AP (Figure 1) was chosen as the prototype because its nonadiabatic dynamics was extensively studied in previous investigation.⁸²

An adaptive learning strategy was used in the construction of the PESs and dynamics simulation. Next, a step-by-step protocol is provided, and more technical details are given in Supporting Information.

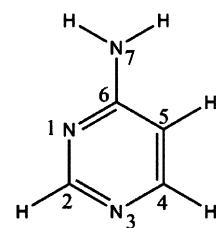


Figure 1. Molecular structure of 6AP and atomic labels.

(1) 100 initial conditions near the S_0 ground-state minimum (GSM) were generated using Wigner sampling at both 0 and 1000 K. The high-temperature (1000 K) sample was used to broaden the sampling space. On-the-fly Born–Oppenheimer molecular dynamics (BOMD) simulations initialized from S_1 were performed based on these initial conditions. The trajectory ran with 0.5 fs time step up to 2000 steps at 0 K (and 100 steps at 1000 K), while some trajectories may crash during the dynamics run. The snapshots in the dynamics run were collected to form our initial data set library (196 754 6AP conformations). A part of this data set was used to build the trial training data set (95 775 6AP conformations). Then, the hierarchical agglomerative clustering algorithm⁴² was used to divide these data into 700 groups. If a cluster contained fewer than 100 geometries, then we selected all of the geometries. Otherwise, we selected at most 100 geometries from each group. All selected geometries formed the first training data set (60 243 6AP conformations). We obtained preliminary PESs of 6AP by the KRR.

(2) Another 50 initial conditions were generated with Wigner sampling at 0 K. The Zhu–Nakamura nonadiabatic dynamics simulation starting from the S_1 state was performed based on the preliminary ML-PESs obtained at Step 1. After the simulation, we obtained the excited-state lifetime and hopping geometries. The CI optimization starting from representative hopping geometries gave us the minimum-energy S_0/S_1 CIs. We constructed the linear-interpolated reaction pathway from S_0 to the CIs based on the ML-PESs and compared them with those obtained using CASSCF method. We found that the ML-PES results are consistent with the CASSCF results, except for the S_1 barrier region caused by the S_2/S_1 crossing. Next, we sampled 30 initial geometries near this region and performed a very short-time dynamics simulation (BOMD: 150 steps) initiated from S_2 , in which the initial velocities were set to 0. We added geometries generated from the short-time dynamics simulation (4254 6AP conformations) into our original data set library. At last, the refined data set library had a total of 201 008 6AP conformations.

(3) A vast number of geometries were selected randomly to define the preliminary training data set. We performed the clustering analysis over these data. Next, we randomly selected the same number of geometries from each cluster to define the final training data set (65 316 6AP conformations) and retrained the PESs again with KRR. The clustering trick largely reduced the computational cost in the training step without losing accuracy.

(4) Because the fitting involves the determination of two parameters, σ and λ , a validation data set (39 971 6AP conformations selected from the data set library) was used to determine them. At the end, the obtained new ML-PESs were used to test their predication ability on the basis of the test data set (61 008 6AP conformations selected from the data set

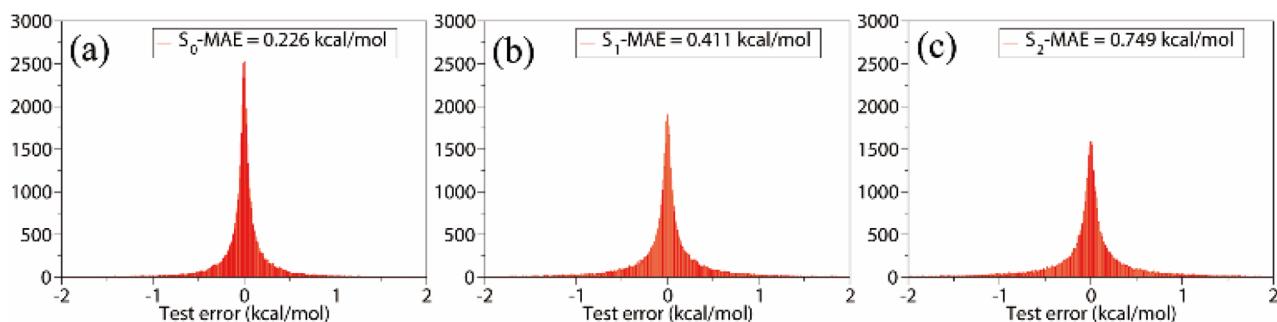


Figure 2. Distributions of the test errors for the adiabatic energy of state (a) S_0 , (b) S_1 , and (c) S_2 based on ML-PESs.

library). Certainly, the training, validation, and test data sets should not have any overlap of the data points.

(5) To check the accuracy of the newly trained ML-PESs, another 100 initial conditions were generated, and the Zhu-Nakamura nonadiabatic dynamics simulation was performed based on both the newly trained ML-PESs and the pure on-the-fly CASSCF PESs. Because the prediction by KRR is an interpolation method, the PESs of a particular geometry can only be correctly predicted if this geometry lies in the sampling area. However, in the dynamics process, some trajectories may go out of the sampling region, which could not be correctly predicted with the KRR method due to its limitation to interpolation prediction. Therefore, for these geometries out of the sampling areas, CASSCF calculations were invoked. In our simulation, such situation is determined by the so-called out-of-confidence geometry that was determined if its CM was not located in the 95% confidence interval calculated with the CMs in the training set. A slightly different idea was suggested in previous work.⁵³ Because the PESs display a double-cone topology in the vicinity of the CI region, the PESs near the CI seam are not smooth functions of the nuclear geometry. The current fitting PESs cannot give a fully satisfied description on such a cusp. To avoid this problem, we switched back to the CASSCF calculation when the energy difference between the different states was <0.1 eV in the dynamics simulations. This approach should help us obtain more reliable results near the CI. The total number of the geometries using the CASSCF results instead of the ML-PESs accounts for 3.9% of all of the geometries in the dynamics simulations.

(6) After we made sure that the ML-PESs worked well, another dynamics simulation with 1000 trajectories was performed based on the ML-PESs. Still, for a few geometries that are out of the reliable confidence interval or are very close to the S_0/S_1 CIs, we switched to the CASSCF calculations.

Before the discussion of the dynamical simulation results based on ML-PESs, we first checked the accuracy of the ML-PESs. Figure 2 shows the distributions of the test errors in the learning procedure for the ML-PESs of 6AP. The mean absolute errors (MAEs) are also presented.

We can see that the ML-PESs accurately predict the energies of all the adiabatic electronic states (S_0 , S_1 , and S_2). Notice that the test errors increase with an increase in the adiabatic electronic state order (with MAE from 0.226 to 0.749 kcal/mol). A possible explanation is because the density of states is very high for the excited states, and even at the Franck-Condon region, different states may strongly mix with each other and the PES crossings are easily formed in the high-dimensional space. These effects result in more nonsmooth areas on the excited-state PES, which further leads to fitting

errors. When the state order increases, such a mixture between different characters becomes stronger, and thus the fitting errors become larger. However, the MAEs are still low enough (<1 kcal/mol) to ensure the possibility of using the ML-PESs on all states involved in the dynamics simulations.

Two CIs, C_2 -CI and C_4 -CI, are responsible for the nonadiabatic decay of 6AP, whose geometries are distinguished by the ring deformation at the C_2 and C_4 atom, respectively. This result is consistent with previous work.⁸² As shown in Figure 3, the potential energy curves of the reaction pathways from the GSM to the two CIs are well predicted using the ML-PESs compared with the CASSCF PESs.

For all states, the potential energy curves based on the ML-PESs and CASSCF are very similar along the reaction pathways, even in the vicinity of the regions where two states come closer. The good performance of the ML-PESs may be attributed by the fact that the BOMD was employed in

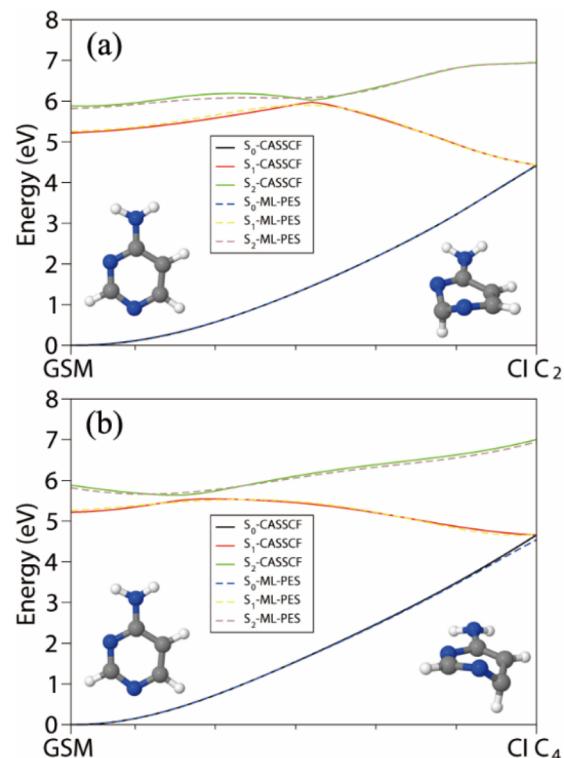


Figure 3. Linearly interpolated reaction pathways from the GSM to (a) C_2 and (b) C_4 CIs based on the CASSCF calculation (solid line) and ML-PESs (dashed line), respectively. All of the GSM and CIs are optimized at the CASSCF level.

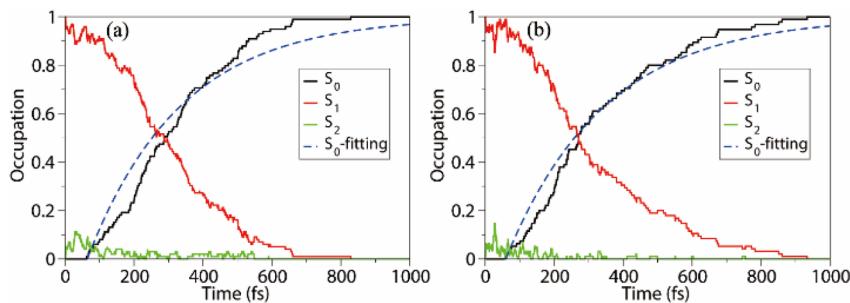


Figure 4. Time-dependent average fractional occupations of the adiabatic electronic states for the Zhu–Nakamura nonadiabatic dynamics with 100 trajectories initiated from S_1 using (a) ML-PESs and (b) CASSCF PESs. The fitting results of the S_0 occupation are also given with dashed lines.

sampling, in which the system accesses the S_0/S_1 CI region several times. However, the double-cone topology of PESs in the branching space may not always be reproduced by the KRR along the whole CI seam. Thus we switched back to electronic structure calculations when the trajectory accesses the CI region in the nonadiabatic dynamics. Note that the additional geometry sampling near the barrier on the S_1 state or S_1/S_2 crossing is also necessary to generate the reliable ML-PESs for reaction pathway calculations and nonadiabatic dynamics simulation.

When the ML-PESs are employed to treat most geometries in the Zhu–Nakamura TSH nonadiabatic dynamics simulation, the time-dependent average fractional occupations of the adiabatic electronic states are shown in Figure 4a. The S_0 time-dependent fractional occupation is fitted by an exponential function, $f(t) = 1 - \exp(-(t - t_a)/t_b)$. The excited-state lifetime is given by $\tau = t_a + t_b$, where $t_a = 64$ fs, $t_b = 271$ fs, and $\tau = 335$ fs, consistent with previous theoretical study with an excited-state lifetime of 416 ± 150 fs.⁸²

The benchmark result based on the on-the-fly dynamics calculations at the CASSCF level is shown in Figure 4b. The time-dependent state occupations agree well with those obtained based on the ML-PESs, even for a small population change in the S_2 state. The excited-state lifetime is also estimated giving $t_a = 60$ fs, $t_b = 287$, and $\tau = 347$ fs. Thus the population dynamics show almost the same excited-state lifetime independent of whether we use the ML-PES or CASSCF PES.

The nonadiabatic dynamics simulations based on our current approach and pure CASSCF PESs provide a similar geometrical distribution at hopping events (Figure 5). Although the former

distribution is slightly broader, it still reproduces the major geometrical features at hopping events in the dynamics process. Clearly, the major reaction channel is via the C_4 –CI, while the secondary channel is governed by the C_2 –CI or the N_3 out-of-plane motion. This result is consistent with previous work.⁸² (Please note that the optimization of the hopping geometries with the N_3 out-of-plane motion will stop at either C_4 –CI or C_2 –CI, which is consistent with previous work.)

Because of the good performance of the ML-PESs in the dynamics simulations, we believe that the ML-PESs in this study are reliable enough for even massive dynamics simulations. Thus the dynamics simulations with another 1000 trajectories were performed, as shown in Figure 6. Compared with the dynamics results with 100 trajectories, a clearer overview of the dynamics feature can be observed, such as a smoother change in the state occupation (Figure 6a) and a clearer distribution of the hopping geometries (Figure 6b).

In many published studies of the TSH dynamics on model PESs,^{22,29,83} a large number of trajectories (generally more than 1000 even 5000) was normally required to ensure fully convergent calculations. This trajectory number implies that the on-the-fly TSH dynamics with 100–200 trajectories basically gives a rather approximated description of the nonadiabatic dynamics of polyatomic systems. If we wish to provide a more reliable description on the final branching ratio comparable to experimental data, then thousands of trajectories or more should be computed.⁸⁴ To improve the statistical accuracy of the TSH dynamics, it is very important to develop reliable approaches to go beyond the current limits of on-the-fly simulations and to compute many more trajectories. The current work provides some useful ideas along this line.

The reliable PES fitting is much more challenging in excited-state dynamics than in ground-state dynamics. Most ground-state molecular dynamics essentially describe the thermal equilibrium distribution. The trajectories often stay in the deep well and exceed the barrier much less, resulting in the good clustering feature in phase space. However, the ultrafast excited-state dynamics is in a highly nonequilibrium state and may also involve strongly distorted geometries, such as a large ring deformation in our current system. The construction of excited-state PESs, which reliably describes the nontrivial geometrical deformation, the low barrier on the flat PES, and the highly nonequilibrium ultrafast dynamics, is not trivial. The current work provides a useful approach to build multidimensional PESs to treat the more general nonadiabatic dynamics of polyatomic systems.

During the last few decades, considerable theoretical efforts were made to develop other rigorous semiclassical dynamics, such as quantum-classical Liouville equations¹⁶ and semi-

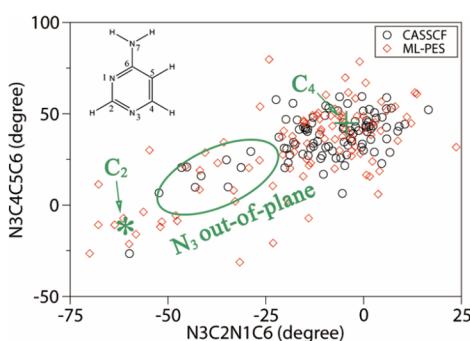


Figure 5. Geometry distributions of the key internal coordinates (dihedral $N_3C_2N_1C_6$ and $N_3C_4C_5C_6$) at hops in the dynamics simulation based on the CASSCF PESs (circle) and ML-PESs (diamond), respectively. The positions of the two CIs (C_2 and C_4) are also given.

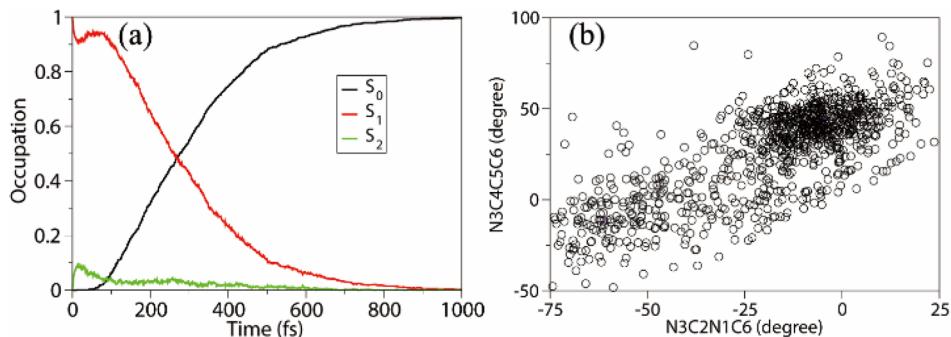


Figure 6. Nonadiabatic dynamics results with 1000 trajectories initiated from S_1 using the ML-PESs: (a) Time-dependent average fractional occupations of the adiabatic electronic states and (b) the geometry distributions of dihedral $N3C2N1C6$ and $N3C4C5C6$ at hops in the simulation process.

classical initial value representation,¹⁵ for a more accurate description of the nonadiabatic dynamics, while these methods normally require a tremendous number of trajectories. Thus the current effort to construct multidimensional PESs opens a new possibility to treat the nonadiabatic dynamics of polyatomic systems with rigorous semiclassical dynamics.

The current work is mainly based on Zhu–Nakamura TSH dynamics. It is more challenging to employ supervised ML approaches to perform Tully's surface hopping dynamics that requires an estimation of the NACVs. For example, it is not trivial to perform the direct fitting of the NACVs by the KRR method because the NACVs change dramatically and even diverge in the vicinity of the CI. In addition, the electronic structure calculations give random sign on electronic wave functions, resulting in an arbitrary sign for the NACVs. Some special tricks have to be used to overcome these problems.⁶¹ This represents an interesting research topic in the future.

In summary, we presented a new approach to perform the nonadiabatic Zhu–Nakamura TSH dynamics simulation using preconstructed PESs based on a ML technique. The 6AP molecule was used as an example. After the proper sampling of the geometries in different important regions and the CASSCF calculations, the KRR method based on the CM descriptor was employed to obtain the PESs, in which adaptive and clustering strategies were also employed in the learning process. The trained ML-PESs display small MAEs (<1 kcal/mol). Then, we employed the ML-PES in the TSH dynamics based on the Zhu–Nakamura algorithm. In the dynamics simulation, the PESs and gradients of most geometries were obtained by the ML-PESs, while we switched to the electronic structure calculations for only a few geometries that were either in the vicinity of the CIs or in the out-of-confidence region. For the 6AP model system, the ML-PES-based nonadiabatic dynamics simulation results, including the excited-state lifetime and reaction channels, were consistent with those obtained using the pure on-the-fly TSH simulation at the CASSCF levels. In addition, a massive dynamics simulation with 1000 trajectories was performed, which provided a much clearer picture of the dynamics process with a reasonable computational cost. This finding suggests that the inclusion of ML-PESs in the nonadiabatic dynamics simulation may allow the computation of a vast number of trajectories with a balance between computational efficiency and accuracy.

COMPUTATIONAL DETAILS

The GSM and vibrational normal modes of 6AP were obtained at the B3LYP/6-31G* level with the Gaussian 09 package,⁸⁵

which were further used to generate the initial conditions (geometries and velocities) of the trajectories based on the Wigner distribution. The SA-CASSCF method was used to obtain the adiabatic energies and gradients. To be consistent with previous study,⁸² the SA-3-CASSCF(10,8) level was chosen in all of the CASSCF calculations of our work. The CASSCF calculations were performed with MOLPRO package.⁸⁶ The on-the-fly surface hopping dynamics simulations based on Zhu–Nakamura theory were performed in our work. Nuclear motion was propagated using the velocity-Verlet algorithm with a time step of 0.5 fs. Three adiabatic electronic states (S_0 , S_1 , and S_2) were involved in the dynamics processes according to a previous study.⁸² All of the dynamics simulations were performed in our developing version of the JADE package.^{39–41} In this package, the module approach was used to combine the dynamics simulation with Fortran and the PES construction with Python. All ML-PES relevant codes, such as KRR, data prescreening, and the interface with dynamics, were written with the Python language, based on the scikit-learn toolkit.⁸⁷ The current work used CM^{46,47,64,88} as the molecular descriptor. It is known that the CM is invariant to the translational and rotational motion of molecules as well as the mirror reflection. However, the CM is not invariant to nuclear permutation. Although the reordering of the CM elements avoids this problem,⁴⁷ the resulting discontinuities in the input feature space may cause problems in the gradient calculations. Thus we still take the original CM as the input descriptor. However, the lack of permutation symmetry should not cause issues in the current work. First, the treatment of the nonadiabatic dynamics of 6AP does not require the consideration of the permutation. Although several identical atoms are found, they will not exchange their positions in the molecular dynamics. The only exception is that two hydrogen atoms in an NH_2 group may exchange their position by torsional motion. However, in excited-state dynamics, such torsional motion should not be very fast. Second, in many complex systems undergoing ultrafast nonadiabatic dynamics, such as the photostability of DNA, photoinduced proton transfer, and photoinduced electron/energy transfer without involving a large geometrical deformation, the permutation is also not relevant. In this situation, we can always use the CM as the molecular descriptor, just like the previous work.⁶⁴ Certainly, when the permutation symmetry is important, more advanced and sophisticated molecular descriptors, such as the symmetry functions,⁴⁹ permutation invariant polynomials,^{89,90} local coordinate,⁹¹ and bag-of-bonds⁹² should be considered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.8b00684](https://doi.org/10.1021/acs.jpclett.8b00684).

Several theoretical methods and additional implementation details, including the Zhu–Nakamura method, molecular descriptors, confidence interval, kernel ridge regression, predictions of potential energies and gradients by the model from KRR, clustering, computational cost, and nonadiabatic dynamics simulation with on-the-fly Tully's surface-hopping method. ([PDF](#))

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Notes

The authors declare no competing financial interest.

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