# Mode-Specific Tunneling Splittings for a Sequential Double-Hydrogen Transfer Case: An Accurate Quantum Mechanical Scheme

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S *Supporting Information*

ABSTRACT: We present the first accurate quantum dynamics calculations of mode-specific tunneling splittings in a sequential double-hydrogen transfer process. This is achieved in the vinylidene−acetylene system, the simplest molecular system of this kind, and by large-scale parallel computations with an efficient theoretical scheme developed by us. In our scheme, basis functions are customized for the hydrogen transfer process; a 4-dimensional basis contraction strategy is combined with the preconditioned inexact spectral transform method; efficient parallel implementation is achieved. Mode-specific permutation tunneling splittings of vinylidene states are reported and tremendous mode-specific promotion effects are revealed; in particular, the CH_2 rock mode enhances the ground-state splitting by a factor of 10^3. We find that the ground-state vinylidene has a reversible-isomerization time of 622 ps, much longer than all previous estimates. Our calculations also shed light on the importance of the deep intermediate well and vibrational excitation in the double-hydrogen transfer processes.

Ground-State Tunneling Splitting $\Delta_0 = 0.013\ cm^{-1}$

Excited-State Tunneling Splitting $\Delta = 14.47\ cm^{-1}$
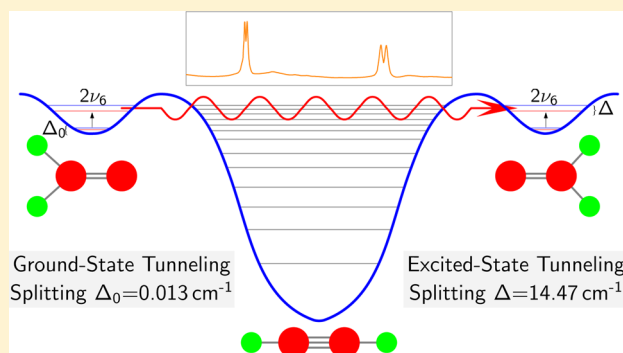
Tunneling splittings, which can provide direct information about hydrogen (H) transfer dynamics and be detected by a variety of high-resolution spectroscopic techniques, are very important observables in many chemical and biological systems and have attracted great interest in recent years.[1−12] Double hydrogen transfer reactions through tunneling are observed in numerous molecular systems, ranging from carboxylic acid dimers[3−5] to DNA chains,[13,14] and roughly speaking, two kinds of underlying H transfer mechanisms can be recognized: concerted and sequential ones. For example, the synchronous concerted double-H transfer is the major mechanism in porphycene,[1,15] whereas the sequential one is believed to be dominant in porphyrin.[16] The tunneling splitting model for the concerted double-H transfer case is similar to that for the single H transfer, which belongs to the classic symmetric double well case, and various approximate methods[1,2,6−12] have been developed for this case. Even very challenging mode-specific tunneling has also been studied for the concerted transfer case; in particular, mode-specific tunneling splittings in porphycene have been calculated[1,15] with approximate methods. However, the sequential double-H transfer case is more interesting and can be very difficult to deal with properly with approximate methods, since the tunneling may be mediated by the intermediate states. The vinylidene−acetylene is the simplest molecular system that exhibits the sequential double-H transfer mechanism, and the tunneling splittings can be produced by tunneling between symmetrically equivalent permutation isomers of vinylidene through the acetylene well (Figure 1).
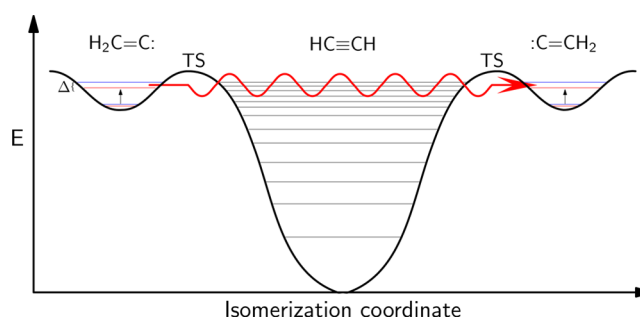
Figure 1. Potential energy profile of the tunneling path between $H_2C=C$: and $:C=CH_2$.

Thus, it can serve as an important model system for studying the double-H transfer. However, despite its small size, it is characterized by large amplitude motions and a deep intermediate well, which supports high density of states.[17] An accurate quantum dynamical (QD) study on the double-H transfer in this system therefore remains an important challenge. Here, we achieve the first accurate QD calculations of mode-specific tunneling splittings for vinylidene vibrational states with an efficient theoretical scheme developed by us, providing a probe to the sequential double-H transfer

isomerization dynamics. Our calculations will play an important role in acquiring a deeper understanding of the tunneling-assisted sequential double-H transfer processes and can provide an useful benchmark for testing various approximate theories before dealing with systems of increased complexity.

So far, very little has been known about tunneling splittings in the benchmark vinylidene−acetylene isomerization system. Experimentally, the earlier finding[18−20] that vinylidene is a very short-lived species may have hindered further efforts in acquiring direct spectroscopic observations of vinylidene tunneling splittings. On the other hand, efforts in search of evidence for acetylene tunneling splittings were made,[17] but they concluded that the splittings were too small (<15 MHz) to be detected by their spectrometer. The vibrational structure of vinylidene was first observed by Lineberger and co-workers using photoelectron spectroscopy in the 1980s,[18] but the spectrum resolution is too low to observe any splitting. More recently, a definitive coulomb explosion imaging (CEI) experimental study[19] was performed by Vager et al., which indicates that vinylidene could be very stable. Consequently, vinylidene may become an excellent candidate for the study of tunneling splittings, and new experiments[21] are being planned to detect the tunneling doublets in vinylidene by Field (private communications). Theoretically, several full-dimensional QD calculations of vinylidene states have been performed by different groups.[22−26] In particular, the Bian group[26] presented very efficient calculations in 2008, in which they acquired basis functions for vinylidene states with a strategy of phase space optimization,[26−28] and extended the implementation of the preconditioned inexact spectral transform (PIST) method[29−31] to a 4-atom molecular system. The present new calculations confirm that Bian group's calculations[26] are the most accurate ones reported in the literature[22−26] (see later discussions). However, all previous calculations are deficient for the study of tunneling splitting, and thus, we need to develop a better theoretical scheme here.

The present theoretical scheme could be referred to as the process-oriented basis function customization (PBFC)-PIST scheme. The PBFC method is a very important technique we propose and its strategy is to customize basis functions for specific physical/chemical process or those desired states by optimizing and adjusting the 1D or nD effective potential. This has the effect of reducing the overall basis size for a given accuracy and greatly increasing the efficiency in the PIST procedures. It should be noted that, this strategy is fully consistent with the PIST method, which is designed toward computing small numbers of eigenstates at a time. In this work, basis functions are customized for the H transfer process we are interested in; a 4D basis contraction scheme[23] is combined with the PIST method and an efficient preconditioner; and the most time-consuming parts of this scheme are parallelized and scale well. Large-scale parallel calculations (the maximum matrix dimension reaches 2 240 000) are performed with this scheme on the global ab initio potential energy surface (PES) developed by Zou and Bowman[32] (or the ZB PES), with all the vibrational states in the energy range of 20 400−23 500 cm^{-1} converged. More details are given below.

We use CC-HH Jacobi coordinates which were chosen first by Bowman et al.[22] (see Figure S1 of the Supporting Information), and the vibrational Hamiltonian ($J = 0$) can be written as

$$\hat{H} = -\frac{1}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{2\mu_0}\frac{\partial^2}{\partial r_0^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2}$$
$$+ \frac{\hat{j}_{12}^2}{2\mu_0 r_0^2} + V(r_1, r_2, r_0, \theta_1, \theta_2, \phi) \tag{1}$$

In eq 1, μ_i ($i = 0-2$) is the reduced mass, $\hat{j}_i$ ($i = 1,2$) is the angular momentum operator associated with r_i, and $\hat{j}_{12}$ is the vector addition of $\hat{j}_1$ and $\hat{j}_2$. In this coordinate system, the full permutation and parity symmetries can be easily exploited.

The present basis function representation is different from what we use in the previous work[26] and can give a much better description of the H transfer isomerization; in particular, a 4D basis contraction strategy[23] is adopted here. To obtain efficient radial discrete variable representations (DVRs),[33,34] the 1D effective potentials for r_1 and r_2 are customized for the H transfer process (details in Figure S2 of the Supporting Information). For the angular coordinates (θ_1, θ_2, ϕ) and r_0, the contraction strategy of Bowman et al.[23] is applied and the contracted bases are eigenfunctions of a 4D effective Hamiltonian

$$\hat{H}^{4D} = -\frac{1}{2\mu_0}\frac{\partial^2}{\partial r_0^2} + \frac{\hat{j}_1^2}{2\mu_1 r_{1e}^2} + \frac{\hat{j}_2^2}{2\mu_2 r_{2e}^2} + \frac{\hat{j}_{12}^2}{2\mu_0 r_0^2}$$
$$+ V^{4D}(r_0, \theta_1, \theta_2, \phi) \tag{2}$$

where r_{1e} and r_{2e} are the equilibrium radial coordinates of vinylidene; $V^{4D}(r_0, \theta_1, \theta_2, \phi)$ is the 4D effective potential, which is the minimal potential optimized with respect to r_1 and r_2, covering both the acetylene and vinylidene regions. These contracted basis functions are able to describe large amplitude motions in these variables but is still oriented toward the H transfer isomerization. The 4D eigenfunction is expanded by the direct product of 3D angular and 1D radial DVR basis functions

$$\Phi^{4D} = \sum_{\alpha}^{N_{r_0}} \sum_{\beta}^{N_{ang}} c_{\alpha\beta}\, \pi_\alpha(r_0) Y_\beta(\theta_1, \theta_2, \phi) \tag{3}$$

where, $\pi_\alpha(r_0)$ is the sine-DVR, and $Y_\beta(\theta_1, \theta_2, \phi)$ is the uncoupled angular basis functions[25,26]

$$Y_\beta(\theta_1, \theta_2, \phi) = \Theta_{j_1-m}(\cos\theta_1)\Theta_{j_2 m}(\cos\theta_2)\cdot\sqrt{\frac{1}{2\pi}}\, e^{im\phi} \tag{4}$$

Here, Θ_{j_1-m} and $\Theta_{j_2 m}$ are normalized associated Legendre polynomials. According to the parity ($\hat{\Pi}$) and permutation ($\hat{P}_{CC}$ and $\hat{P}_{HH}$) symmetries, the primitive angular base can be divided into eight categories.[22,23] In this work, we calculated the totally symmetric A_1' states, whose angular bases require that the quantum numbers j_1 and j_2 be even, and the parity be "+"; and the B_2' states (antisymmetry with respect to $\hat{P}_{CC}$), for which the quantum number j_1 is changed to be odd. With the symmetry-adapted angular base, the 4D Hamiltonian matrix elements can be evaluated by eq S1 (Supporting Information), and the resultant eigenvalue problem is solved with the PIST method.

The total wave function is expanded as

$$\Psi = \sum_{i}^{N_{r_1}} \sum_{j}^{N_{r_2}} \sum_{k}^{N_{4D}} d_{ijk}\, \pi_i(r_1)\pi_j(r_2)\Phi_k(\theta_1, \theta_2, \phi, r_0)$$

$$(5)$$

In terms of the basis expansion, we separate the basis functions into the inner (r_1 and r_2) and outer (θ_1, θ_2, ϕ, and r_0) groups, and the expression of Hamiltonian matrix elements is given in eq S2 (Supporting Information), resulting in a large, sparse, and well-structured matrix. Herein, the PIST method combined with an optimal separable basis plus Wyatt (OSBW) preconditioner[31,35,36] is employed to solve its eigenvalue problem. To make large-scale computations possible, message passing interface (MPI) is utilized to parallelize the most time-consuming parts of this scheme, which include the evaluation of Hamiltonian matrix elements, block Jacobi diagonalization and quasi-minimal residual iterations, and very good scalability is achieved. In the Supporting Information (page S5), a detailed description of the parallel strategies in our PBFC-PIST/OSBW code is given. It is worth mentioning that, Poirier et al. performed some pioneering work on the parallelization of the PIST method,[37,38] and in this work, a step forward is achieved in parallelizing the OSBW preconditioning, which evidently reduces the number of linear solver iterations. Both the 4D and 6D calculations are carried out with the PIST/OSBW method, and the calculational details are described in the Supporting Information (page S7), including the coordinate ranges, basis sizes and PIST/OSBW computational details (Supporting Information Table S1), which have been carefully examined to converge all the reported states.

To characterize the computed eigenstates, we follow the method proposed by Zou and Bowman[23] and analyze the wave functions by inspecting the expectation values of r_2 and r_0, as shown in Figure 2. Because the coordinates r_2 and r_0 are
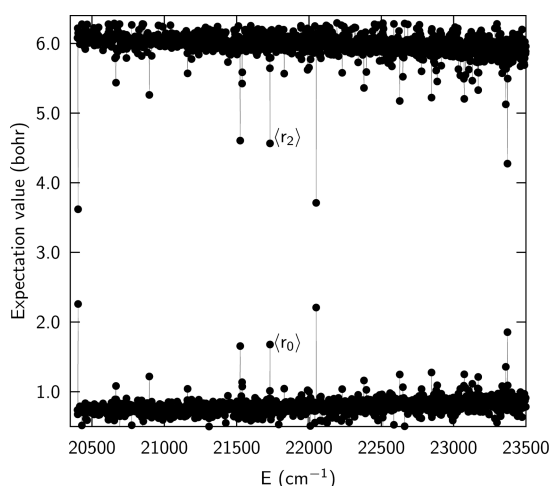
Figure 2. Expectation values of r_2 and r_0 for the A_1' states in the energy range of 20 400−23 500 cm^{-1}, computed with the basis size $N_{r_1} = 25$, $N_{r_2} = 32$, and $N_{4D} = 2800$. Energies are relative to the acetylene minimum.

drastically different for the vinylidene and acetylene equilibrium geometries, their expectation values $\langle r_2 \rangle$ and $\langle r_0 \rangle$ are very useful in distinguishing between the eigenstates. We see that almost all of the eigenstates are highly excited acetylene states ($\langle r_2 \rangle > 5.7$ and $\langle r_0 \rangle < 0.8$ bohrs); several convex states correspond to the vinylidene states ($\langle r_2 \rangle < 5.0$ and $\langle r_0 \rangle > 1.2$ bohrs). To make definite assignments of these vinylidene states, we propose an

easy and effective method, that is, plotting the wave function against each vinylidene normal coordinate, and more details are given in the Supporting Information (page S9).

The convergence of the A_1' and B_2' vinylidene states with the increase of basis sizes is examined carefully by a series of large scale parallel calculations, and some typical results are shown in Figure 3. Here, the basis size notation (25, 32, 2800) denotes that $N_{r_1} = 25$, $N_{r_2} = 32$, and $N_{4D} = 2800$. We see that very good convergence is achieved; in particular, highly converged results are obtained for the ground state, which are necessary to converge the tiny tunneling splitting as small as 0.013 cm^{-1}. The largest dimension of Hamiltonian matrix used in our calculations exceeds 2×10^6, and to the best of our knowledge, this is much larger than those used in all previous calculations for the vinylidene−acetylene system. In addition, some computed acetylene states are extracted as well and are found to be in reasonable agreement with those from previous calculations,[24,39−41] which indicates that the acetylene side of isomerization can also be well described with our scheme.

In brief, we find that highly converged energy levels of vinylidene vibrational states, necessary for the study of tunneling splittings, can be obtained with the basis size (25, 32, 2800), which are reported in Table 1, along with the experimental values and other theoretical results. We see from Table 1 that the experimental energy levels from photoelectron spectroscopy[18] are basically reproduced by our calculations, though the experimental resolution is too low for the splitting, and the remaining small deviations should come from the ab initio ZB PES[32] used in our QD calculations. The vinylidene zero point energy (ZPE) obtained in this work is very close to that reported in our previous vinylidene vibrational calculations[26] but is much lower than those reported in other theoretical calculations[23−25] (see Figure 4). To clarify the convergence problem, we have performed some test calculations, and we find that when we increase the 4D basis size N_{4D} from 500 to 1000, the computed vinylidene ZPE decreases from 20 414 cm^{-1} down to 20 404 cm^{-1} quickly. This implies that Carrington group's calculations[25] are actually not fully converged because $N_{4D} = 640$ is used and the value of 20 414.8 cm^{-1} is reported in their work. In view of the small basis size Bowman et al.[23] and Tennyson et al.[24] used (<50 000), it is unlikely for their calculational results to reach the level of convergence required for tunneling splitting. However, it should be mentioned that Bowman et al.[23] carried out some very limited calculations on the B_2' states of vinylidene, and a very rough splitting of 2 cm^{-1} was estimated for the ground state. Although Bian group's previous vinylidene vibrational calculations[26] are found to be more accurate than other calculations reported in the literature (see Figure 4), a careful comparison of the vibrational energy levels with the present calculations indicates some differences, which result from the fact that the H transfer isomerization can not be described by the old theoretical scheme.

The tunneling splittings can be produced by tunneling between the two carbon permutation isomers of vinylidene through the acetylene well (see Figure 1). Hence, the vinylidene vibrational energy levels should consist of closely spaced doublets, and in the present case, the A_1 symmetric states will split into two branches: A_1' and B_2'. Then, the accurate mode-specific tunneling splittings Δ can be easily obtained from energy levels of the A_1' and B_2' states, and are presented in Table 1. Table 1 shows that, the splitting for the vinylidene
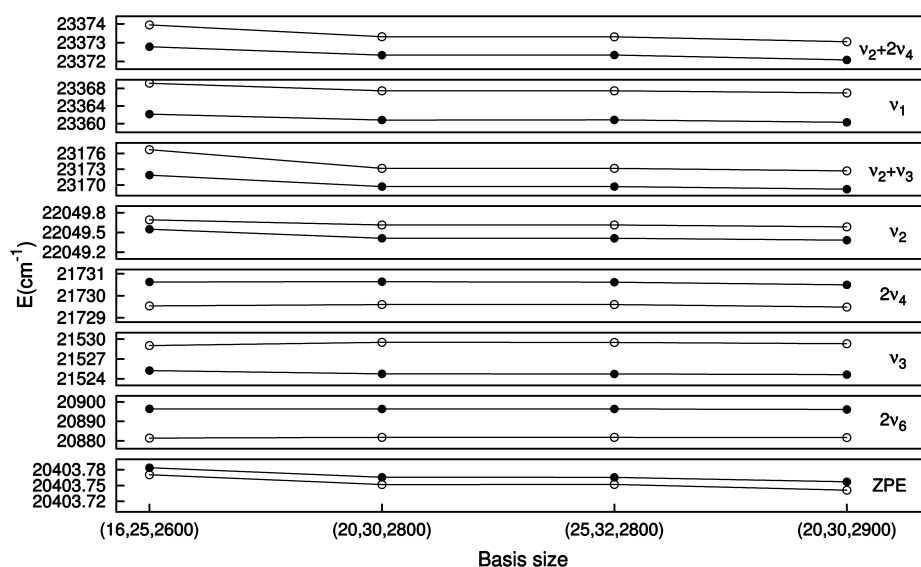
Figure 3. Convergence of the A_1' (solid dot) and B_2' (hollow dot) vinylidene vibrational energy levels with the increase of basis sizes. Energies are relative to the acetylene minimum.

Table 1. Our Calculated Mode-Specific Tunneling Splittings of Vinylidene Vibrational States[a], the Ratio Δ/Δ_0, and the Isomerization Lifetimes[b] in Comparison with the Resonance Decay Lifetimes[c,d]

states	vibrational type	$E_{B_2'}$[e]	$E_{A_1'}$[e]	expt[f]	Δ	Δ/Δ_0[g]	t[h]	τ[i]
ZPE		20403.7521	20403.7655		0.0134	1	622	302
$2\nu_6$	CH_2 rock	478.060	492.516	450 ± 30	14.472	1080	0.58	0.104
ν_3	CH_2 scissors	1125.771	1120.969	1165 ± 10	4.789	357	1.74	1.087
$2\nu_4$	out of plane	1325.847	1326.855		1.021	76	8.16	5.38
ν_2	CC stretch	1645.863	1645.647	1635 ± 10	0.203	15	41.07	16.85
$\nu_2 + \nu_3$	CC stretch and CH_2 scissors	2769.425	2765.961	2800 ± 30	3.451	258	2.42	1.39
ν_1	CH symmetric stretch	2963.703	2957.057	3025 ± 30	6.633	495	1.26	0.683
$\nu_2 + 2\nu_4$	CC stretch and out of plane	2969.561	2968.581		0.967	72	8.62	2.319

[a]Δ in cm^{-1}. [b]t in ps. [c]τ in ps. [d]Energy levels (E in cm^{-1}) of the A_1' and B_2' vinylidene states are also listed, along with the experimental values. The basis size used is $N_{r_1} = 25$, $N_{r_2} = 32$, and $N_{4D} = 2800$. [e]The vinylidene ZPE is relative to the acetylene minimum, and energies for the vibrationally excited states are relative to the corresponding vinylidene ZPE. [f]Available experimental values from ref 18. [g]Δ_0 is the tunneling splitting of the ground state. [h]The isomerization lifetime is defined as the average tunneling passage time from vinylidene to acetylene deduced from the tunneling splitting. [i]Full-dimensional quantum dynamics calculations of vinylidene resonance decay lifetimes from ref 36.
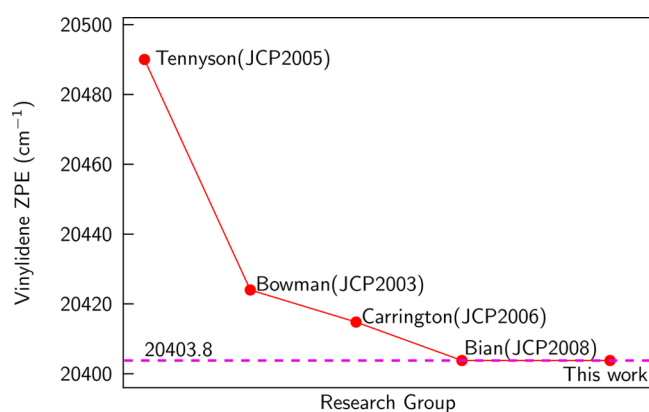
Figure 4. Comparison of the vinylidene zero point energies (ZPEs) calculated by different groups.[23−26] Energies are relative to the acetylene minimum.

ZPE is very small (only 0.013 cm^{-1}), which is considerable smaller than that of any excited state. It is very challenging to converge such a small splitting and to ensure a higher accuracy in our calculations, the ground-state energy eigenvalue is

computed separately, with the energy shift put at 20 403 cm^{-1} in the window, and the Lanczos convergence criterion set at 10^{-8} cm^{-1}. From the ratio Δ/Δ_0, we see that the excitation of different vibrational modes enhances the ground-state splitting by a factor of 10 to 10^3, indicating remarkable mode-specific promotion effects. Generally speaking, the promotion effects are observed for all the vibrationally excited states and the vibrational modes closely related with the vinylidene−acetylene isomerization have larger tunneling splittings. In particular, the $2\nu_6$ excited state has the largest tunneling splitting of 14.47 cm^{-1}, about 1080 times of that for the ground state and such strong enhancement effect has not been observed before. This extraordinary phenomenon is understandable because it is well known that the CH_2 rock (the Q_6 mode) is the main isomerization coordinate[42,43] in the double-H transfer process. In addition, the Q_3 (CH_2 scissors) and Q_1 (CH symmetric stretch) modes also make significant contributions to the isomerization,[43] as a result of which, considerable tunneling splittings of 4.789 and 6.633 cm^{-1} are obtained for the ν_3 and ν_1 states, respectively. Furthermore, the normal modes Q_2 (CC stretch) and Q_4 (out of plane) are less relevant to isomerization, and accordingly, the ν_2 and $2\nu_4$ states show far less

strong promotion effects, which are by factors of 15 and 76, respectively.

The tunneling splittings of eigenstates revealed in our calculations encode H-transfer dynamics, and we can adopt the simple dynamical model of system coherent oscillation back and forth among the three vinylidene/acetylene wells (see Figure 1). This provides a new interpretation on the surprising phenomenon found in the CEI experiment,[19] that both vinylidene-like and acetylene-like molecular geometries are observed at 3.5 μs after the production of vinylidene. Although a single eigenstate can have a lifetime longer than 3.5 μs, our results also suggest that 3.5 μs is not the reversible isomerization lifetime of vinylidene. Here, according to $t_p = h/\Delta$, the tunneling period t_p can be deduced from the splitting, and because one period of the oscillation process involves twice of the sequential double-H transfer, the average tunneling passage time from the vinylidene to acetylene wells should be $t_p/4$, which is viewed as the isomerization lifetime of vinylidene. The mode-specific isomerization lifetimes obtained in this way are also presented in Table 1, in comparison with the "resonance decay" (RD) lifetimes calculated before.[36] The RD lifetime actually involves an ideal physical model, which presumes that vibrationally highly excited acetylene levels can be dealt with as a quasicontinuum. The computed RD lifetimes thus provide us with useful lower bounds to the realistic isomerization lifetimes. In fact, highly excited acetylene levels are found to be not so dense, and that is why the isomerization lifetimes shown in Table 1 are much larger than the RD lifetimes. In particular, the ground-state vinylidene is found to have an isomerization lifetime of 622 ps, which is about twice of the recently reported RD lifetime of 302 ps,[36] or the earlier RD lifetime of 293 ps obtained in Köppel's 5D QD calculations.[44,45] This is a very important single result that indicates that the ground-state vinylidene is quite stable. Table 1 also shows that, the mode-specific isomerization lifetimes are fully consistent with the corresponding mode-specific RD lifetimes. It is encouraging that now we are able to go beyond the dense eigenstate approximation and report the isomerization lifetimes of vinylidene, which are much more realistic than what were known before.

In summary, accurate mode-specific tunneling splittings for a sequential double-H transfer case are reported for the first time. We have performed the largest quantum dynamics calculations (the maximum matrix dimension reaches 2 240 000) ever made for the benchmark vinylidene−acetylene system, and highly converged results are obtained for the carbon permutation tunneling splittings of vinylidene. This is achieved with an efficient PBFC-PIST theoretical scheme developed by us and by a high-performance parallel implementation of this scheme. The promotion effects of vibrational excitation and deep intermediate well are revealed. Our results indicate remarkably strong mode-specific effects, where excitation of different vibrational modes enhances the ground-state splitting by a factor of 10 to 10^3; in particular, the tunneling splitting of the CH_2 rock mode is about 1080 times larger than that for the ground state. The vinylidene isomerization lifetimes are deduced from the splittings, which go beyond the dense eigenstate approximation used in all previous calculations, and the comparison with the RD lifetimes provides an internal consistency check. New high-resolution and state-resolved experimental measurements on permutation tunneling splittings of vinylidene are highly desirable. It is our hope that the present work can extend our understanding of the tunneling-assisted sequential double-H transfer processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The CC-HH Jacobi coordinates, 1D effective potentials for r_1 and r_2, expression of the Hamiltonian matrix elements, a detailed description of the parallel strategies in our PBFC-PIST/OSBW code, calculational details, and the assignment of vinylidene states. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00672.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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