Multidimensional H Atom Tunneling Dynamics of Phenol: Interplay between Vibrations and Tunneling

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ABSTRACT: Multidimensional facets of the hydrogen tunneling dynamics of phenol excited in \( S_1 \) (\( \pi\pi^* \)) have been unraveled to give particular \( S_2 \) vibronic states strongly coupled or actively decoupled to the O–H tunneling coordinate. Strong mode-dependent variation of the tunneling rate measured with picosecond lasers indicates that tunneling probability is extremely sensitive to low-frequency vibrational modes seemingly orthogonal to the O–H elongation coordinate unless the rate of energy randomization exceeds that of tunneling. The multidimensional nature of tunneling has also been manifested in efficient internal-to-translational energy transfers observed at \( S_1 \) vibronic modes strongly coupled to the tunneling coordinate, giving insights into otherwise the formidable multidimensional map of tunneling process. The nonadiabatic bifurcation dynamics in the later stage of the chemical reaction has been disentangled by analyzing picosecond time-resolved product state distributions, resolving a long controversial issue regarding the origin of high or low kinetic energy component of the product translational energy distributions.

INTRODUCTION

Tunneling is one of the most intriguing quantum mechanical phenomena and at the same time ubiquitous in nature. A particle enforced to reside inside the potential well with finite height and width has always nonzero probability of escaping even when its energy is much below the barrier height. Although quantum mechanical and/or semiclassical calculations have been extremely helpful in explaining a vast number of experimental results to date, the tunneling process is certainly still beyond our full understanding especially for polyatomic molecular systems where the tunneling is not a simple one- or two-dimensional problem anymore. For recent decades, as a prototypical model system for tunneling, the photochemistry of phenol has been intensively studied both theoretically and experimentally.\(^{1-28}\) As phenol belongs to one of the most important chemical and biological building blocks, its photochemistry and physics have been subjects of great interests for many years. The first excited state of phenol is an optically bright \( \pi\pi^* \) bound state (\( S_1 \)) whereas the upper-lying second excited state has the character of \( \pi\sigma^* \) (\( S_2 \)) which is unbound with respect to the O–H elongation coordinate. The \( S_1 \) and \( S_2 \) states become degenerate at the multidimensional nuclear configuration, tunneling dynamics in terms of barrier height, width, and detailed shape should be treated in the multidimensional nuclear configurational space.

The lifetime of 2.0–2.5 ns at the \( S_1 \) zero-point level of phenol has been estimated from the previous spectroscopic and time-resolved studies.\(^{14,17,31-34}\) From the literature,\(^{35}\) the quantum yield of tunneling had been estimated to be \( \sim 0.83 \), indicating that the H atom tunneling rate should be \( \sim 4 \times 10^8 \) s\(^{-1}\), whereas the sum of other pathways’ rates such as fluorescence and intersystem crossing is \( \sim 1 \times 10^8 \) s\(^{-1}\). This is consistent with the previous experimental finding that the D fragment from tunneling is little produced from the \( S_1 \) zero-point level of phenol-d\(_6\) (\( C_6D_5OD \)) whereas its lifetime is \( \sim 12.5 \) ns.\(^{36}\) Namely, the O–D tunneling process is almost theoretically predicted to be located \( \sim 6000 \text{ cm}^{-1} \) above the \( S_1 \) minimum energy point.\(^{3,22-25}\) This energetic location of the \( S_1/S_2 \) conical intersection is quite high compared to the energy given to the system through the Franck–Condon window of the \( S_1-S_0 \) optical excitation. Therefore, the \( S_1 \) phenol at the zero-point level is strongly bound with respect to the O–H elongation. Although the barrier height given by MECI energetics in one-dimensional configuration is presumed to be very high, the barrier has theoretically been predicted to be quite thin along the O–H elongation coordinate.\(^{22}\) Furthermore, as tunneling process is not restricted to the one-dimensional configuration, tunneling dynamics in terms of barrier height, width, and detailed shape should be treated in the multidimensional nuclear configurational space.

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Figure 1. State-specific rate measurement of phenol. (a) Ps (1 + 1′) R2PI spectrum (red) overlaid with ns result45 (black) with mode assignments.46,47 (b) R2PI spectrum in full range of the excitation energy. The experimental pump−probe scheme is displayed in the inset. (c) Time constants estimated from fits to state-specific transients of C₆H₅OH⁺ (open circles). Appearance rates of H⁺ (filled circles) are obtained from analyzing high KE region (13.2−18.7 kcal/mol) of time-resolved velocity-map ion images at selective vibronic excitations. Literature values are given from high-resolution studies (square),29,30 ps pump−probe (inverse triangle) at the S₁ zero-point level,14 fs pump−probe (open and filled triangles),17 and very recent ps pump−probe parent transients (rhombi).34 Inset: Multidimensional concept for tunneling is depicted. Depending
on the coupled geometry of vibronic mode (polar angles of arrows), the tunneling path (arrows) could be shortened (coupled) or lengthened (decoupled) across classically forbidden region of phase space (closed space between $S_1$ and $S_2$ surfaces). Completely blocked due to the H/D primary isotope effect in phenol-$d_6$, while its nonradiative decay rate of $\sim 8 \times 10^7$ s$^{-1}$ is not much influenced by the OH/OD substitution. Such a large kinetic isotope effect has been observed for other molecular systems undergoing the H atom tunneling, including methylamine, pyrrole, or catechol. Full dimensional calculations of tunneling rate could roughly reproduce the lifetime of phenol whereas very interesting theoretical idea has been recently proposed that the relative long lifetime of the $S_1$ phenol is due to the destructive interference between two bifurcated reactive fluxes encircling the conical intersection with different phase changes. In the latter, Guo and colleagues could reproduce the experiment quite well for the excited-state lifetime of phenol at the $S_1$ origin and predicted tunneling rates for several $S_1$ vibronic modes of phenol and phenol-$d_6$, although the experimental verification seems to be nontrivial at the present time (vide infra). The previous femtosecond (fs) pump–probe study by the Stavros group has shown that the directly measured excited-state lifetime of phenol is 2.5 ns at the $S_1$ zero-point level and it is consistent with the appearance rate of the H fragment only at or near the zero-point level. They reported that the appearance rate of H fragment remains more or less constant even when the excitation energy exceeds 3000 cm$^{-1}$ above the $S_1$ origin, taking this as the clear evidence for the H atom tunneling since the internal energy given to the vibrational modes orthogonal to the O–H elongation coordinate would otherwise speed up the dissociation reaction. However, as the fs laser pulse is intrinsically too much wide in terms of its energetic window, it was not trivial to invoke any vibronic mode dependence of the tunneling rate, which is indispensable for the description of the tunneling process beyond the one-dimensional picture. Herein, we have measured tunneling rates of the individual $S_1$ vibronic states by employing the picosecond (ps) pump–probe method where energetic and temporal resolutions are simultaneously satisfied for the spectroscopic separation and the lifetime measurement of each vibronic state. The strong mode dependence of reaction rate has been observed, indicating not only that the tunneling of the $S_1$ phenol should be treated in the multidimensional configurational space but also that even very low frequency modes seemingly orthogonal to the O–H elongation coordinate influence the tunneling rate quite significantly (vide infra). The product appearance rates are found to be same as the $S_1$ state lifetimes, differing from the previously reported fs work. In addition to the ps transients of parent and fragment, the total translational energy distributions of products have been obtained as a function of the reaction time, giving the clear evidence that both the slow and fast components of the H fragment have the same origin of tunneling though their detailed paths in the later stage of reaction are bifurcated afterward. This work puts an end to the long controversial issue regarding the origin of the slow kinetic energy components of fragments of phenol.

**EXPERIMENTAL SECTION**

Experimental methods have been given elsewhere recently, and some changes are only briefly described here. Ps pump–probe laser pulses were generated starting from the 1 kHz synchronized fs/fs Ti:sapphire regenerative amplifier system seeded with a fs oscillator (Legend Elite-USP/P, Vitara-T-HP, Coherent). Tunable ultraviolet frequencies for pump/probe wavelengths were obtained by the nonlinear mixing of pulses from two optical parametric amplifiers (TOPAS-800 ps, Light Conversion) pumped by the 50:50 split fundamental outputs. A pump laser pulse ($\lambda_1 = 277-246$ nm) was used for the vibronic state-specific excitation in the $\pi\pi^*$ state, whereas probe laser pulses were used to detect the decay of reactant $C_6H_5OH^*$ ($\lambda_2 = 245/280/301$ nm) or growth of photoproduct H$^*$ ($\lambda_2 = 243.1$ nm for the $(2 + 1)$ resonance ionization via 2s). Two pulses were nearly collinearly aligned, and focused on the gas mixture in the pulsed supersonic jet with plano-convex spherical lenses ($f = 300$ mm) for the H$^*$ velocity map imaging (VMI). For $C_6H_5OH^*$ detection, pump and probe laser beams were used without focusing. Polarizations of both laser beams were parallel with the position sensitive detector. When parent ion transients were taken, a $\lambda/2$ waveplate was employed to rotate the polarization axis of the probe laser pulse so that polarization angle between pump and probe is $54.7^\circ$ (magic angle) in order to rule out any rotational dephasing effect. The entrance window of the chamber was 1 mm thick. The temporal delay between pump and probe pulses ($\Delta t$) were scanned from $\sim 20$ ps to the temporal limit of 2.85 ns by employing the double-pass alignment scheme using a broadband hollow retroreflector (UBBR2.5–1UV, Newport) mounted on a computer-controlled 220 mm optical delay line (DDS220, Thorlabs).

Phenol (Sigma-Aldrich) was heated to 60 °C, bubbled with 2 bar of neon carrier gas, and expanded into vacuum through a nozzle orifice operated by a 200 Hz pulsed Even-Lavie valve before it was skimmed through a 2 mm diameter skimmer. The imaging spectrometer consists of two differentially pumped vacuum chambers. Source and ionization chambers were evacuated with two turbo-molecular pumps with the pumping rates of 2300 and 800 L/s (HiPace 2300/800, Pfeiffer Vacuum), respectively, while each foreline was pumped by a dry pump (ACP 40G/28G, Alcatel). The conventional VMI electrodes accelerate ions through a 30 cm-long time-of-flight region to a two-dimensional position-sensitive detector equipped with Chevron-type microchannel plates (MCP) backed by a P46 phosphor (Photonis). For VMI measurements, a pulsed voltage gate was applied to MCP with the high voltage pulse generator (PVX-4140, DEI) to select a specific mass-to-charge ratio of the ion. The ion spots on the phosphor screen were captured by a triggered CMOS camera (GS3-U3-3254, PointGrey) for each event. Each camera image was processed with the area threshold condition in order to avoid hot-pixel contribution and accumulated in the event-counting mode, then reconstructed three-dimensionally with the polar onion peeling (POP) method. The measured kinetic energy distributions were calibrated with the one-color (2 + 1) resonance-enhanced ionization of xenon at 250 nm. For the time-resolved VMI (TR-VMI) experiment, a series of ion images were obtained during the same acquisition time at each time-delay point. At each delay position, images were recorded for 5 s. Data were collected by scanning the translation stage...
spectroscopic studies,14,17,31 pulses, Figure 2. Consistently with the previous time-resolved instance, the lifetime gets slightly decreased to delay time between pump (S1 are obtained by monitoring the parent ion as a function of the parent transients for unambiguously identi

324 cm−1 of 112, 0.99 ns at 935/938 cm−1 (112), 0.99 ns at 935/938 cm−1 (11 and 4110b1), and 2.1 ns at 975 cm−1 (9a1), Figures 1 and 2. When the internal energy is

τ ∼ 2.7 ns at 3474 cm−1 (16a2), 0.57 ns at 3974 cm−1 (16a), 0.99 ns at 3974 cm−1 (410b), and 1.08 ns at 3974 cm−1 (16b), Figures 1 and 2. When the internal energy is

Figure 2. ps time-resolved parent transients measured at each vibronic state excitations. Distinct tunneling rate at each vibronic mode could be clearly notified from the comparison with the transient of τ ≈ 2.27 ns at the S1 zero-point level (red dashed line). For each vibronic mode, normal mode displacement vectors are depicted for the S1 geometry optimized with planar constraint from time-dependent density functional theory (B3LYP/aug-cc-pVDZ) calculations. For full sets of decay transients, see Figures S2 and S3.

RESULTS AND DISCUSSION

In Figure 1, the ps (1 + 1′) resonance two-photon ionization (R2PI) spectrum of phenol in the supersonic jet shows well-resolved S1 vibronic features. Individual vibrational modes have been appropriately assigned according to previous meticulous spectroscopic studies.46 Notably, the mode assignment for the 324 cm−1 band had been controversial in terms of whether or not it belongs to hot band. Since hot bands are little observed in the extremely low-temperature supersonic jet used here, we adopt here the more recently reported 112 (Wilson notation) mode assignment37 for the 324 cm−1 band. Now ps-resolved parent transients for unambiguously identified vibronic states are obtained by monitoring the parent ion as a function of the delay time between pump (S1−S0) and probe (D0−S1) laser pulses, Figure 2. Consistently with the previous time-resolved spectroscopic studies,4,6,17,31−34 the lifetime (τ) at the S1 origin of phenol is found to be ∼2.3 ns. However, quite surprisingly, the S1 lifetime shows huge fluctuations in the low excitation energy range up to its S1 internal energy of ∼1200 cm−1. For instance, the lifetime gets slightly decreased to ∼1.9 ns at 324 cm−1 of 112 whereas it even increases to ∼2.9 ns at 374 cm−1 of 16a2. Large lifetime fluctuations continue to give τ ∼ 2.2 ns at 475 cm−1 (6a1), 1.1 ns at 523 cm−1 (6b1), 1.3 ns at 783 cm−1 (121), 0.99 ns at 935/938 cm−1 (11 and 410b), and 2.1 ns at 975 cm−1 (9a1), Figures 1 and 2. When the internal energy is larger than 1200 cm−1, the S1 lifetime shows little variation with increasing the excitation energy and gradually decreases to give τ ∼ 800 ps at ∼3600 cm−1. Incidentally, it is intriguing to note that the lifetime of S1 phenol at one quantum of the OH stretching mode had been calculated to be ∼880 ps,23 even though our experimental value of ∼800 ps at ∼3600 cm−1 does not necessarily mean that the tunneling rate is increased due to the OH stretching mode excitation. Rather, considering that the tunneling process is much slower than the rate of intramolecular vibrational redistribution (IVR) which is presumed to be activated from the internal energy of 1200 cm−1, the experimentally measured lifetimes in the high internal energy region (> ∼1200 cm−1) should reflect those of the states of which energies are randomized among isoenergetic quantum states dispersed along many vibrational degrees of freedom. Therefore, in this circumstance, mode dependence of the tunneling rate observed within the S1 internal energy of 0–1200 cm−1 region totally makes sense as the corresponding bright zeroth-modes maintain their own characteristics during the tunneling process. It should be noted that a part of this work, ps time-resolved parent transients of phenol at selected wavelengths, has been independently carried out by Lai et al. and recently reported.34 Although our experimental results and interpretation are quite different from those of ref 34 in many aspects, Figure 1, any critical comparison has not been made here at the present time.

Notably, H atom tunneling of phenol is found to be accelerated by two-times when the S1 vibronic mode of 6b, 12, or 1 (and 4 + 10b) is excited. These modes belong to in-plane vibrations, and thus no obvious correlation between the mode characters and tunneling rates could be found as long as symmetry is concerned, even though a slight decrease of the tunneling lifetime at 324 cm−1 (112) might be attributed to the degeneracy breaking of the conical intersection along the out-of-plane vibrational coordinate. As a matter of fact though, the experimental finding that the tunneling rate gets even slightly slower at 374 cm−1 (16a2) than that of the origin indicates that
there is indeed no consistent rule of thumb for the mode- dependence of the tunneling rate in terms of the symmetry property of vibrational mode. As tunneling occurs in the multidimensional configurational space, lowering or thinning of the effective adiabatic H atom tunneling barrier due to avoided crossing for the reactive flux excited along these vibrational degrees of freedom could be conceived as one of the reasons. In addition to this general and yet routine explanation, one may give the more explicit description from the experimental observation as below. Namely, fast components of total translational energy distributions obtained by the velocity map ion imaging (VMI) of H fragment show sudden blue shifts when the 12 and 1 (and 4 + 10b) vibronic modes are excited, though the direction of shift is same but its magnitude is less standing out for the 6b mode (523 cm$^{-1}$), Figure 3. The most probable translational energy of products at the internal energy of 783 (121) or 935/938 (11 and 4110b1) cm$^{-1}$ increases by $\sim$1.0 kcal/mol compared to one obtained at the origin or 475 (6a1)c m$^{-1}$. Remarkably, the translational energy distribution shifts back to that of the S1 origin at the 9a mode of 975 cm$^{-1}$ where the tunneling rate is slowed down again by two times to give $\tau \approx 2.1$ ns compared to $\tau \approx 0.99$ ns.

Figure 3. State-selective H$^+$ time-resolved VMI results. (a) Plot of total kinetic energy release (TKER) distributions (5-point averaged) at the S1 zero-point level as a function of the pump–probe time delay time (total 31 time steps). (b) Background-subtracted TKER distribution by subtracting the time-zero distribution corresponding to prompt H$^+$ formation by multiphoton excitation. Inset: raw H$^+$ image at the longest time delay of 2.85 ns. (c) Time-resolved product translational energy distributions at the S1 zero-point level and (d) those obtained at the 12$^1$ vibronic mode excitation. (e) One of total product translational energy distributions obtained at selected vibronic modes presented in left columns of three boxes in the bottom. TKER distribution at the delay time of 2.85 ns (open circles) is well described by the combination of a Gaussian function centered at $\sim$7 kcal/mol and another asymmetric Gaussian function centered at $\sim$16 kcal/mol (see Figures S6 and S7 for more details). Vertical dash-dotted lines (sky-blue) represent the position of the most probable kinetic energy of products at the S1 zero-point level. Notable shifts of the experimental peak positions relative to this line reflect the change of energy disposal dynamics in tunneling process (see the text). Also broadening of the translational energy distribution with increasing the excitation energy is easily notable from the comparison to the distribution measured at the S1 zero-point level (orange dash-dotted lines). (f) Fragment transients for the fragment of which the kinetic energy is distributed over 13.2–18.7 kcal/mol (blue squares) and those for the fragment in the low kinetic energy region of 3.4–8.9 kcal/mol (red circles) with fits. Same time constants reproduce the experiment for both high- and low-energy fragments. Similar transients at different vibronic modes are shown in right columns of three boxes in the bottom. Distinct H$^+$ appearance rate for each vibronic band is clearly notable from the comparison with transients at the S1 zero-point level ($\tau \approx 1.94$ ns, dashed orange).
measured at the just slightly lower excitation energy of 935/938 cm\(^{-1}\). It is also noteworthy that the most probable translational energy even decreases by \(~1.0\) kcal/mol compared to that of the \(S_1\) origin when the 374 cm\(^{-1}\) (16a\(^2\)) mode of \(\tau \approx 2.9\) ns is excited. Product translational energy distributions do not shift gradually with increasing the internal energy; those of the \(S_1\) origin and 6a mode are identical whereas those of 12 and 1 and 4 + 10b modes are almost same as well. This experimental observation suggests that the internal energy given by 12 or 1 and 4 + 10b mode transforms into translational energies of products quite efficiently in the tunneling process. Mode excitation of 11\(^2\), 6a or 9a, on the other hand, may lead to its mode conservation as a spectator\(^{15}\) throughout the reaction or it could be transformed into different mode excitations of products, as evidenced by the experimental fact that its corresponding translational energy distribution is little changed from that of the \(S_1\) origin, Figure 3. Even though the vibrational modes in the Franck–Condon region are hardly expected to be conserved throughout the whole reaction pathway, it should be noted that the vibrational modes associated with these spectators of \(S_1\) phenol are either conserved or more excited in the \(C_6H_5O\bullet (\tilde{X})\) product according to the reports by Ashfold and colleagues\(^{7,15}\), which is amazingly consistent with our experimental findings. According to them, 16a mode of \(C_6H_5O\bullet (\tilde{X})\) is highly excited at many excitation energies, and it was suggested that 16a is the major coupling mode which facilitates the \(S_1\)–\(S_2\) tunneling especially in terms of its \(a_2\) vibrational symmetry.\(^{7,15}\) And yet, both the parent and fragment transients do not show any increase in the tunneling rate when 16a\(^2\) mode is excited. Rather, as above, the tunneling rate gets even slowly slowed down to give \(\tau \approx 2.9\) ns compared to that of the \(S_1\) origin. Furthermore, the translational energy of product at 16a\(^2\) decreases from that of the \(S_1\) origin, Figure 3. This indicates that the 16a mode is indeed somewhat strongly associated with the tunneling coordinate but in a way to deter the tunneling process and instead induce the internal excitation of the corresponding mode. The 16a mode, therefore, may be an active-decoupling mode in the tunneling process, in a sense that corresponding vibrational oscillation makes the reactive flux stay longer in the bound \(S_1\) potential well thus being excited along the 16a mode when it finally escapes to \(S_2\) via tunneling.

The consistent positive correlation between tunneling rate and kinetic energy release indicates that 12, 6b, and 1 and 4 + 10b modes are strongly coupled to the O–H tunneling coordinate. In other words, the tunneling path of phenol is not restricted to a simple O–H elongation coordinate, as one can easily expect for polyatomic systems. Rather, the multidimensional tunneling path, although it is nontrivial to be uniquely defined, is facilitated when strongly coupled modes such as 12, 6b, and 1 and 4 + 10b are excited, giving the faster tunneling rate and the more efficient internal-to-translational energy transfer. Shortest tunneling paths of reactive fluxes excited at the specific \(S_1\) vibronic modes are indeed diverse in the multidimensional nuclear configurational space, and the dynamic behaviors observed here at well-identified and not-randomized vibronic modes shed light on the multidimensional nature of tunneling dynamics. When the excitation energy is more than \(~1200\) cm\(^{-1}\) above the \(S_1\) origin, the tunneling rate shows a monotonic increase with the increase of excitation energy with little specific mode dependence. As mentioned above, this is most likely due to the fast IVR in \(S_1\) taking place prior to the relatively slow tunneling process. This rather early energy randomization as well as the narrow Franck–Condon window hampers experimental verification of theoretical predictions made for the mode effect on the tunneling rate of the \(S_1\) phenol\(^{25}\). Despite these complex and difficult situation of polyatomic molecules, however, strong mode-dependence of tunneling rates as well as kinetic energy releases observed here provides the invaluable insights into the multidimensional tunneling dynamics.

One of the controversial issues in the photodissociation dynamics of phenol is the origin of the slow component in the product translational energy distribution. In Figure 3, as similarly found in many previous other works\(^{7,15,17,26}\) there exist two distinct kinetic energy components in the total translational energy distribution of products. The high-kinetic energy component of which the shape adopts a Gaussian-type function should represent the reactive flux underwent the prompt O–H bond rupture along the repulsive \(S_1\) state and then tunneling from \(S_0\) followed by the nonadiabatic transition at the \(S_0/\tilde{S}_2\) conical intersection to reach the final \(C_6H_5O\bullet (\tilde{X}) + H\) fragments. Meanwhile, the low kinetic energy component appears to have the rather statistical character of high internal and low kinetic energies for the final fragments. In this work, as mentioned earlier, the translational energy distribution of the H fragment has been measured as a function of the reaction time, which is equivalent to the delay time between pump and probe laser pulses. According to our spatiotemporal analyses for time-dependent VMI images, the appearance rate of the H fragment responsible for the fast component is identical to the one comprising the slow component. It should also be noted that time constants of the parent-decay and product-appearance at each vibronic state are consistent in terms of their quantitative values, although the product appearance rate is systematically overestimated compared to the parent decay rate in a single-exponential fitting procedure partly due to the small but persistent background contribution in the former due to the multiphoton excitation (see Figure S5). Despite multiphoton background signals, most of the H fragment signal in the experiment is from the one-photon excitation of phenol for both the high and low kinetic energy components, Figure 3.

The ratio of fast and slow components in the product translational energy distribution remains more or less constant for all excitation energies studied in this work. This strongly indicates that both the slow and fast components originate from the H atom tunneling of the bound \(S_1\) phenol. Namely, if the slow component originates from internal conversion or intersystem crossing from \(S_1\) to \(S_0\) or \(T_1\), respectively, the fast/slow ratio of kinetic energy components would have been strongly influenced by the largely fluctuating tunneling rates over the quite narrow energy range where the rate of competing processes of internal conversion or intersystem crossing should remain more or less constant. It should be noted, however, that our product state distributions are measured at the reaction time of \(~2.85\) ns and thus much slower rising fragments with the lifetimes longer than \(~1\) \(\mu\)s are not detectable as pointed out in the recent report by the Ni group.\(^{26}\) Therefore, one cannot exclude the potential contribution of the unimolecular reaction channel from the vibrationally hot \(S_0\) state prepared from the direct internal conversion from \(S_1\). Nonetheless, the slow component of the translational energy distribution observed at the reaction time of \(~2.85\) ns, Figure 3, is quite significant and its origin needs to
be identified. The tunneled reactive flux rides on the repulsive $S_2$ state before it bifurcates at the $S_0/S_2$ conical intersection in the later stage of the reaction, Figure 4. A portion of the reactive flux undergoes the nonadiabatic transition to give the H fragment and $\text{C}_6\text{H}_5\text{O}• \bullet$ radical ($\tilde{X}$), maintaining the characteristics of the impulsive nature of fragmentation on the repulsive surface. Meanwhile, the adiabatic channel giving the $\text{C}_6\text{H}_5\text{O}• \bullet$ radical ($\tilde{A}$) is energetically blocked as the energy given to the $S_1$ phenol, for instance, at the origin is below the energetic threshold of the upper corresponding channel. Therefore, the other portion of the reactive flux should be bounced back to the $S_0/S_2$ conical intersection region and then it could leak into the $S_0$ ground state with a finite probability. Thereafter, finite or complete energy-exchange in $S_0$ may occur, followed by the dissociation reaction on the ground adiabatic state to give the low-translational and high-internal energy distribution of products. In other words, significant portion of the flux may be “trapped” in the upper adiabatic well above the $S_0/S_2$ conical intersection and thereafter bifurcates into two distinct pathways of either (i) continuous riding on the repulsive $S_2$ or (ii) going back to $S_0$ for dissociation on the lower adiabatic surface located below the $S_0/S_2$ conical intersection.

Kinetically, one can propose that tunneling from $S_1$ to $S_2$ is the slow rate-determining process, for instance, with a rate constant of $k_0$ whereas subsequent bifurcation into two different channels leading to either the fast or slow kinetic energy component of product should be relatively faster with associated rate constants of $k_1$ and $k_2$, respectively. In the latter, appearance rates of both fast and slow kinetic energy components in the second stage are governed by the sum of $(k_1 + k_2)$ while their relative yields are determined by the ratio of $(k_1/k_2)$. Therefore, the mode-dependent variation of tunneling rate $(k_0)$ does not influence the branching ratio of fast and slow components of final products, which is quite consistent with our experimental observation. Even though $k_0$ could be directly estimated from ms measured from ps transients of parent, quantitative estimations of $k_1$ and $k_2$ are nontrivial as the bifurcation kinetics is ironically overwhelmed by the much slower tunneling rate. However, from the fast/slow component ratio of ~2:1, one can estimate that $k_1$ may be approximately two times larger than $k_2$. It is most likely that the reactive flux responsible for the slow component of the translational energy distribution does not undergo the complete energy exchange with quite dense vibrational hot $S_0$ states in the Franck–Condor region. Rather, as the $S_0/S_2$ conical intersection is located at the extended O–H bond distance, it is quite plausible for the reactive flux to experience only limited phase space before it reaches to final products in the asymptotic limit. Actually, the shape of the slow component is hardly explained by the Boltzmann-type function only. Rather, the exit barrier of the lower-lying adiabatic potential surface under the $S_0/S_2$ conical intersection could have been reflected in the kinetic energy release dynamics for the slow component.

**CONCLUSIONS**

Herein, hydrogen atom tunneling dynamics of the $S_1$ phenol has been state specifically investigated by the ps time-resolved velocity-map ion imaging method to give state-selective tunneling rates as well as time-resolved product state distributions. In the $S_1$ internal energy region where the given internal energy is not randomized yet, the tunneling rate is found to be strongly mode-dependent, indicating that the tunneling path from the bound $S_1$ ($\pi\pi^*$) to repulsive $S_2$ ($\sigma\sigma^*$) is indeed multidimensional in nature. Vibrionic modes strongly coupled to the tunneling path are identified as the extent of coupling has been manifested by the increase of tunneling rate as well as the more efficient internal-to-translational energy transfer during the tunneling process. Nonadiabatic bifurcation dynamics at the $S_0/S_2$ conical intersection following the H atom tunneling is found to dictate the kinetic energy release of final fragments. Major portion of the reactive flux sliding on $S_2$ undergoes the nonadiabatic transition at the $S_0/S_2$ conical intersection to give the H + $\text{C}_6\text{H}_5\text{O}• \bullet$ ($\tilde{X}$), maintaining the characteristics of the impulsive nature of $S_2$. Meanwhile, the other portion of the reactive flux bounces back to the $S_0/S_2$ conical intersection region and the O–H dissociation occurs on the adiabatic surface below the $S_0/S_2$ conical intersection to give the low-translational and high-internal energy distribution of products. Multidimensional tunneling dynamics of polyatomic molecules are formidable to understand, and yet our experimental findings in the tunneling dynamics of phenol here has thrown new light on complex predissociation mechanism of excited states, also motivate lots of challenging theoretical tasks.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b00327.

Picosecond (1 + 1’) R2PI and H$^+$ photofragment excitation (PHOFEX) spectra, full results of time-resolved ion yield (TR-IY) at individual vibronic bands with several different probe wavelengths, full result of H$^+$ time-resolved velocity map ion images (TR-VMI), analysis on multiphoton background TR-VMI signals, table of state-specific decay and growth rates, details in the TKER deconvolution procedures, and estimation of $(k_1 + k_2)$ (PDF)

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