Mode-dependent H atom tunneling dynamics of the $S_1$ phenol is resolved by the simple topographic view of the potential energy surfaces along the conical intersection seam

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Junggil Kim, Kyung Chul Woo, and Sang Kyu Kim

AFFILIATIONS
Department of Chemistry, KAIST, Daejeon 34141, Republic of Korea

$^a$Present address: Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore.

$^b$Author to whom correspondence should be addressed: sangkyukim@kaist.ac.kr

ABSTRACT

Mode-dependent H atom tunneling dynamics of the O–H bond predissociation of the $S_1$ phenol has been theoretically analyzed. As the tunneling is governed by the complicated multi-dimensional potential energy surfaces that are dynamically shaped by the upper-lying $S_1(\pi\pi^*/S_2(\pi\sigma^*)$ conical intersection, the mode-specific tunneling dynamics of phenol ($S_1$) has been quite formidable to be understood. Herein, we have examined the topography of the potential energy surface along the particular $S_1$ vibrational mode of interest at the nuclear configurations of the $S_1$ minimum and $S_1/S_2$ conical intersection. The effective adiabatic tunneling barrier experienced by the reactive flux at the particular $S_1$ vibrational mode excitation is then uniquely determined by the topographic shape of the potential energy surface extended along the conical intersection seam coordinate associated with the particular vibrational mode. The resultant multi-dimensional coupling of the specific vibrational mode to the tunneling coordinate is then reflected in the mode-dependent tunneling rate as well as nonadiabatic transition probability. Remarkably, the mode-specific experimental result of the $S_1$ phenol tunneling reaction [K. C. Woo and S. K. Kim, J. Phys. Chem. A 123, 1529–1537 (2019)] (in terms of the qualitative and relative mode-dependent dynamic behavior) could be well rationalized by semi-classical calculations based on the mode-specific topography of the effective tunneling barrier, providing the clear conceptual insight that the skewed potential energy surfaces along the conical intersection seam (strongly or weakly coupled to the tunneling reaction coordinate) may dictate the tunneling dynamics in the proximity of the conical intersection.

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INTRODUCTION

The $\pi^*$-mediated photochemistry has been both extensively and intensively investigated for recent many years to reveal the dynamic effect of the conical intersection on the nonadiabatic dynamics. It is highly relevant to the adiabatic and/or nonadiabatic leakage of the flux of the electronically excited state, which is particularly important in understanding of the ultrafast process of the non-radiative relaxation of the biological molecules, hydrogen/proton transfer, or photo-isomerization. Accordingly, a number of model systems including a variety of chemical derivatives of phenols, thiophenols, anisoles, pyrroles, or thioanisoles have been tackled for interrogating the nonadiabatic dynamics taking place in the vicinity of the conical intersections encountered along the relaxation and/or reaction pathways. Among those, the H atom tunneling dynamics of the $S_1$ phenol is one of the most-studied systems. Rydberg-tagging H atom translational spectroscopy on the O–H bond predissociation of the $S_1$ phenol by the Ashfold et al. has provided the very detailed energy disposal dynamics resulting from the nonadiabatic couplings among the close-lying $S_0$, $S_1(\pi\pi^*)$, and $S_2(\pi\sigma^*)$ states. The $S_1$ phenol dynamics has also been theoretically investigated for the energy disposal dynamics as well as the tunneling rate on the high-level ab initio potential energy surfaces (PESs). Despite that the overall dynamics in
terms of the vibronic couplings involved in the energy partitioning and tunneling are seemingly well understood through the quite intensive studies to date, the mode-specific dynamic outputs such as the vibrational mode-dependent tunneling rates (which is quite dramatic from the recent experiment\textsuperscript{28}) are far from being understood thoroughly.

It should be emphasized that the S\textsubscript{1} vibronic states are well identified in the low internal energy range where the mode-randomization is not turned on yet, indicating that the characteristics of the individual vibrational modes are retained over the whole lifespans of the corresponding modes.\textsuperscript{29} This provides the unique opportunity to explore many different regions of the potential energy surfaces especially in the vicinity of the conical intersection.

At the planar geometry where the O–H moiety is on the same plane as the phenyl moiety, the S\textsubscript{1}/S\textsubscript{2} and S\textsubscript{0}/S\textsubscript{2} conical intersections are encountered along the O–H bond extension coordinate (Fig. 1). The S\textsubscript{1} vibronic states excited in the vertical S\textsubscript{1}–S\textsubscript{0} excitation window are spectroscopically well resolved and their normal modes have been properly assigned.\textsuperscript{30} Lifetimes associated with the individual S\textsubscript{1} vibronic modes have been very precisely determined recently by the picosecond time-resolved transients.\textsuperscript{31} The S\textsubscript{1} lifetime of phenol has been measured to be ~2.3 ns at the zero-point vibrational energy level (ZPVL), whereas the quantum yield of the H atom tunneling reaction has been estimated to be ~0.8.\textsuperscript{32} This indicates that the H atom tunneling reaction rate should be ~4 times faster than the rate of the other nonradiative decay channel such as internal conversion. Therefore, the H atom tunneling reaction is most responsible for the S\textsubscript{1} state relaxation of phenol. The reactive flux tunneled through the barrier under the S\textsubscript{0}/S\textsubscript{2} conical intersection slides down on the repulsive S\textsubscript{2} state before it funnels through the second S\textsubscript{0}/S\textsubscript{2} conical intersection nonadiabatically or adiabatically to give the C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}O radical in the ground state (X) or excited state (A), respectively, in the later stage of the reaction. As the C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}O (A) channel is energetically not accessible for most of the low-energy S\textsubscript{1} vibronic levels, the adiabatic reactive flux is actually bounced back to S\textsubscript{0} momentarily to give the H fragment of the low translational energy. Nonadiabatic transition probability, energy disposal dynamics, and tunneling rates had been experimentally measured, and they should provide crucial information regarding the PESs near the conical intersections. For instance, it had been found by the Ashfold group that the progression of the odd quanta of the out-of-plane torsional mode (v\textsubscript{36}) is highly excited in the nascent C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}O(\tilde{X}) product, indicating that the nonadiabatic coupling at the S\textsubscript{1}/S\textsubscript{2} and/or S\textsubscript{0}/S\textsubscript{2} conical intersections exerts the flux to excite the out-of-plane vibrational mode (a\textsuperscript{12}u\textsuperscript{+} symmetry) of the final fragment.\textsuperscript{33–35} Theoretically, the saddle point of the adiabatic PES has been reported to be located at the C–O–H dihedral torsional angle of 20\textdegree,\textsuperscript{36–38} demonstrating that the out-of-plane mode is indeed strongly coupled to the reaction coordinate as it is parallel to the derivative coupling vector at the branching plane of the S\textsubscript{1}/S\textsubscript{2} conical intersection.\textsuperscript{36–38}

Not surprisingly though, the dynamic effect of the conical intersection extended along the remaining (3N – 8) seam coordinates has not been much spotlighted as it is not anticipated to largely influence the tunneling reaction taking place underneath the conical intersection. Unexpectedly, however, the significant dynamic effect of the conical intersection seam has recently been demonstrated in the H atom tunneling dynamics of trans-ortho-cresol.\textsuperscript{41} Namely, the internal rotation of the CH\textsubscript{2} moiety (on the ortho-position to the OH moiety), as one of the (3N – 8) conical intersection seam coordinates, gives the three-fold periodic modulation of the PES with a barrier of ~400 cm\textsuperscript{-1} along the conical intersection seam coordinate. This leads to the dramatic modulation of the effective tunneling barrier along the CH\textsubscript{3} internal rotor angle, providing the perfect explanation for the sharply varying state-specific tunneling rates observed in the very narrow excitation energy range of the multiple internal rotor quantum states. This experimental fact observed in the dynamics of trans-ortho-cresol strongly indicates that the conical intersection seam coordinates should be taken into account properly as the topography of the multi-dimensional PES could be strongly modified by the extension along the seam coordinates. In this regard, we have explored the multi-dimensional PES at the conical intersection extended along the seam coordinates associated with the particular vibrational modes of interest to rationalize the previously reported experiment of the mode-specific tunneling rate of the S\textsubscript{1} phenol as well as the mode-specific energy disposal dynamics.\textsuperscript{40,41} Particularly, we have employed a simple model where the PES along the O–H bond extension (tunneling) coordinate is extended into the additional dimension of the specific vibrational normal mode displacement coordinate. It turns out that the topography of the consequent two-dimensional PES at the conical intersection could explain the mode-specific tunneling rate of the S\textsubscript{1} phenol extremely well. Despite the simplicity of our model compared with the previous other sophisticated theoretical studies,\textsuperscript{25,26} the current work may provide a simple yet conceptually interesting aspect of the tunneling reaction taking place under the multi-dimensional conical intersection skewed along the seam coordinates.

![FIG. 1. Schematic potential energy curves of phenol in the planar geometry for the lowest three singlet electronic states along the O–H bond extension coordinate. Nonadiabatic H atom tunneling takes place through the potential energy barrier under the first S\textsubscript{1}/S\textsubscript{2} conical intersection (S\textsubscript{1}/S\textsubscript{2} CI), whereas the reactive flux on the repulsive S\textsubscript{2} potential bifurcates at the second S\textsubscript{0}/S\textsubscript{2} conical intersection (S\textsubscript{0}/S\textsubscript{2} CI) into the C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}O radical in the ground state (X) or the C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}O radical in the excited state (A).](image-url)
Computational details

To get the topography of the PES along the tunneling coordinate, the vertical excitation energies have been calculated at the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) level with the aug-cc-pVDZ basis sets (Gaussian 09). The rigid-body scan of the one-dimensional potential energy curve along the O–H bond extension coordinate is obtained from the optimized minimum energy structure of \( S_1 \) at the O–H bond length \( R(\text{OH}) \) of 0.97 Å. The following three critical points along the tunneling coordinate are chosen for further calculations: the \( S_1/S_2 \) conical intersection \( (R(\text{OH}) = 1.19 \text{ Å}) \), the classical (outer) bound of the tunneling barrier \( (R(\text{OH}) = 1.70 \text{ Å}) \), and the \( S_0/S_2 \) conical intersection \( (R(\text{OH}) = 2.20 \text{ Å}) \). The potential energy curve at the inner bound \( (R(\text{OH} \sim 1.10 \text{ Å}) \) with respect to the orthogonal vibrational coordinate is expected to be little different from that calculated at the \( S_1 \) equilibrium point \( (R(\text{OH} \sim 0.97 \text{ Å}) \) as the \( S_1 \) state between \( R(\text{OH}) = 0.97 \) and that of 1.10 Å is deeply bound with respect to the O–H bond extension. The one-dimensional potential energy curves (PECs) at four fixed O–H bond lengths are then obtained by rigid scans along the several mass-weighted \( S_1 \) vibrational normal mode displacements. The topographic shape of each PEC reflects how the specific vibrational mode is coupled to the tunneling coordinate at different stages of the tunneling reaction.5,6,49 A series of PECs along the tunneling coordinate for the particular vibrational mode excitation gives the overall topographic shape of the reaction pathway in terms of the effective tunneling barrier heights (and widths) as well as their variations with the different vibrational mode excitations. This way, one could realize that the seemingly (or frequently conjectured) orthogonal vibrational normal modes are not necessarily perpendicular to the tunneling reaction coordinate as their couplings to the reaction coordinate are evolved along the chemical reaction pathway (vide infra). It should be emphasized here that the mode-randomization is quite slow in the low internal energy range (0–1200 cm\(^{-1}\)), and thus, the initial vibrational mode excitation of the \( S_1 \) phenol is retained during its whole lifespan. This has been validated in previous experiments5 and belongs to one of the basic premises of the whole dynamic description given in this work.

RESULTS AND DISCUSSION

The state-specific tunneling rates of the \( S_1 \) phenol show the dramatic mode-dependent fluctuations.45 For instance, the \( S_1 \) lifetime is shortened to be \( \sim 0.99 \text{ ns} \) at the \( \nu_1 = 1 \) excitation of 935 cm\(^{-1}\), indicating that the tunneling rate increases more than twice compared with that of \( \tau \sim 2.27 \text{ ns} \) at ZPL. This highly contrasts with the lifetime of \( \sim 2.10 \text{ ns} \) measured at the \( \nu_9 = 1 \) excitation of 975 cm\(^{-1}\), as well as the energy difference between \( \nu_1 \) and \( \nu_9 \) modes is just \( \sim 40 \text{ cm}^{-1}\). This experiment already suggests that the \( \nu_1 \) mode may be strongly coupled to the tunneling coordinate, whereas the \( \nu_9 \) mode remains orthogonal to the reaction coordinate as a spectator. As both \( \nu_1 \) and \( \nu_9 \) modes belong to the in-plane mode, the \( S_1/S_2 \) conical intersection should be evolved into the degenerate seam coordinates along the configurational changes associated with those modes, although this argument is based on the conjecture that the normal mode coordinates calculated at the \( S_1 \) minimum could be used to describe the molecular structures at the \( S_1/S_2 \) conical intersection. In other words, the \( S_1/S_2 \) conical intersection seam has been constructed here along the normal mode coordinates calculated at the \( S_1 \) minimum. In fact, the gradient difference vector of the \( S_1/S_2 \) conical intersection of phenol has been reported to be the combination of O–H and C–O bond stretching displacements,60 which is apparently orthogonal to the \( \nu_1 \) or \( \nu_9 \) mode. Topography of the one-dimensional PEC with respect to the \( \nu_1 \) normal mode displacement at the nuclear configuration of the \( S_1/S_2 \) conical intersection is found to be quite different from that calculated at the \( S_1 \) minimum. Namely, the minimum energy point at the \( S_1/S_2 \) conical intersection with respect to the \( \nu_1 \) mode is significantly shifted by \( \sim 0.08 \text{ a.u.} \) from that corresponding to the \( S_1 \) minimum energy configuration. As illustrated in the lower trace of Fig. 2, this indicates that the effective tunneling barrier \( \Delta E_{\text{barrier}}(Q) \) may be substantially lowered when the reactive flux is spread toward the positive direction with respect to the \( \nu_1 \) normal mode displacement according to the relation \( \Delta E_{\text{barrier}}(Q) = \Delta E_{\text{CI}}(Q) - \Delta E_{\text{Eq}}(Q) \), where \( \Delta E_{\text{CI}}(Q) \) or \( \Delta E_{\text{Eq}}(Q) \) represents the energy profiles along the normal mode \( (Q) \) at the \( S_1 \) minimum or \( S_1/S_2 \) conical intersections, respectively. Therefore, the conical intersection extended along \( \nu_1 \) might give the effectively lower tunneling barrier for the \( S_1 \) reactive flux prepared at the first quantum of the \( \nu_1 \) mode compared with that at ZPL. Although the effective tunneling barrier gets a bit higher along the opposite displacement of the \( \nu_1 \) mode, the reaction should be governed by the faster process with the lower tunneling barrier. In the adiabatic picture, therefore, the experimental finding of the tunneling rate increased on the \( \nu_1 \) mode excitation is well rationalized as the effective tunneling barrier is lowered due to the tilted shift of the conical intersection seam along the \( \nu_1 \) normal mode displacement. For the \( 9a \) mode, on the other hand, the topography of the PEC at the \( S_1/S_2 \) conical intersection is found to be little different from that calculated at the \( S_1 \) minimum along the corresponding normal mode displacement (Fig. 2), giving the only tiny shift of \( \sim 0.01 \text{ a.u.} \). The almost identical topographic shapes of PECs at \( S_1 \) minimum and \( S_1/S_2 \) conical intersection configurations thus suggest that the tunneling barrier along the O–H bond extension coordinate would not be altered by the vibrational excitation of the \( \nu_9 \) mode. This is again quite consistent with the experiment of \( \tau \sim 2.10 \text{ ns} \) found for the \( \nu_9 \) mode excitation of the \( S_1 \) phenol.36 In this regard, it might be fair to state that the tunneling coordinate is strongly coupled to the \( \nu_1 \) mode, whereas it is only weakly coupled to the \( \nu_9 \) mode during tunneling through the multidimensional barrier below the \( S_1/S_2 \) conical intersection from the topographic perspective of the potential energy surfaces at critical points along the O–H extension coordinate.

To get a more intuitive picture of the mode-specific couplings in the vicinity of the conical intersection, we have calculated the nuclear configurations of the conical intersection seam on the two-dimensional PES with respect to the O–H bond extension and the \( \nu_1 \) (or \( \nu_9 \)) normal mode displacement coordinates, Fig. 3. In the two-dimensional PES, the \( S_1/S_2 \) conical intersection seam has been obtained by the interpolation of the degenerate crossing points of \( S_1 \) and \( S_2 \). Intriguingly, the \( S_1/S_2 \) conical intersection seam projected onto the two-dimensional coordinates of the O–H bond length and \( \nu_1 \) normal mode displacement is largely skewed toward the shortened (lengthened) O–H bond length with the positive (negative) displacement of the \( \nu_1 \) vibrational normal mode, Fig. 3(a). Incidentally, this may be depicted by the parabolic cross-section of a harmonic cone cut by the tilted plane. In another aspect, it should be noted that the coupling between two modes (e.g., the mixing of
FIG. 2. (Upper trace) Potential energy curves calculated with respect to the 1 (left) or 9a (right) normal mode displacement coordinate at the optimized geometries at the $S_1$ minimum (EQ, open blue circle) or $S_1/S_2$ conical intersections (CI, open red triangle). The calculated data points are smoothly connected using the quartic polynomial functions (solid lines). The normalized displacement vectors of the 1 or 9a vibrational normal mode are depicted. (Lower trace.) Variation of the effective tunneling barrier height calculated from the relation of $\Delta E_{\text{barrier}}(Q) = E_{\text{CI}}(Q) - E_{\text{EQ}}(Q)$ plotted as a function of the 1 (left) or 9a (right) normal mode displacement (see the text).

The O–H bond extension and $v_1$ on the $S_1/S_2$ conical intersection seam could be the consequence from that the $v_1$ mode (which is the eigenvector of the Hessian matrix of $S_1$) is not necessarily the eigenvector of $S_2$. As the O–H bond length is supposed to be little changed along the $v_1$ normal mode displacement vector, as manifested in the straight vertical line of the projection of the $S_1$ minimum configuration onto the two-dimensional PES, the skewed seam coordinate of the $S_1/S_2$ conical intersection indicates that the $v_1$ mode is strongly coupled to the O–H extension coordinate to facilitate the tunneling process through the shaping of the PES along the seam coordinate. This also suggests that the adiabatic tunneling barrier, as shaped by the skewed conical intersection seam, moves into the more reactant-like nuclear configuration by the $v_1$ mode excitation. For the $v_{9a}$ mode excitation, on the other hand, the projection of the conical intersection seam onto the two-dimensional PES along the O–H bond extension and the $v_{9a}$ normal mode displacement coordinates shows the little-skewed (nearly) straight vertical line [Fig. 3(b)], indicating that the $v_{9a}$ mode remains as the orthogonal mode to the O–H bond extension coordinate even at the $S_1/S_2$ conical intersection seam. This conforms to the one-dimensional PEC along the $v_{9a}$ normal mode displacement calculated at the fixed O–H bond length of the conical intersection in Fig. 2. Namely, the effective tunneling barrier is not influenced by the $v_{9a}$ mode excitation. This is quite consistent with the experimental tunneling lifetime of $\sim 2.10$ ns found for $v_{9a}$, which is more or less the same as $\tau \sim 2.27$ ns at the ZPL of the $S_1$ phenol (vide supra).

The mode-specific tunneling probability could now be estimated from the semi-classical calculations using the Wentzel–Kramers–Brilluion (WKB) approximation. In fact, it has been suggested by Guo et al. that adiabatic models would be inappropriate for nonadiabatic tunneling calculations in the proximity of the conical intersection where the geometric phase effect as well as the diagonal Born–Oppenheimer correction should be properly invoked. In this regard, the WKB calculation in this work does not warrant the quantitative prediction of the tunneling probability of the $S_1$ phenol. However, the dynamic behavior of the tunneling rate with varying the $S_1$ vibronic mode of phenol (as manifested in the experiment) could be at least qualitatively rationalized by the semi-classical model employed here, especially because most of the vibrational modes of interest are parallel to the degenerate seam coordinates of the conical intersection. Namely, the nonadiabatic tunneling correction (which is expected to be most significant with respect to the gradient and coupling vectors on the branching plane) would be more or less equally influential to the tunneling rate for the vibrational modes laid along the nearly degenerate seam coordinates. The one-dimensional WKB tunneling probability is given as follows:

$$P = \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{+\infty} e^{-\frac{(x - c)^2}{2\hbar^2}} dx,$$

where $c$ is the classical turning point and $\hbar$ is the reduced Planck constant.
The adiabatic PEC modulated along Q is rather complicated in nature as manifested in the skewed conical intersection seam coordinate (Fig. 3) due to the strong mode-coupling during the tunneling process. Just for simplicity, only the height of the effective adiabatic tunneling barrier adjusted along Q at the fixed conical intersection configuration has been taken into account in the \( P_{1D,WKB}(Q) \) calculation (see the supplementary material). The \( S_1 \) lifetime at the specific vibronic mode excitation is derived from the equation of \( \tau = (\nu_{OH} \cdot P_{WKB})^{-1} \). The resultant \( S_1 \) lifetimes calculated by the tunneling probability at the excitations of the \( \nu_1 \) or \( \nu_9 \) mode are listed in Table I, giving an extremely satisfactory explanation of the experiment in light of the very simple adiabatic semi-classical model used here. It should be noted that the \( S_1 \) lifetimes calculated at ZPLs of the individual vibrational modes are all different as each \( S_1 \) lifetime is obtained by the weighted average of the ZPL wave function of a specific vibrational mode only. The qualitative trend of the tunneling rate with the vibrational mode excitation should be thus judged from the comparison of the \( S_1 \) lifetime of \( n = 0 \) to that of \( n = 1 \) (or 2) of the identical vibrational mode. For instance, the \( S_1 \) lifetime of 2.14 ns calculated at \( n = 0 \) of the \( \nu_1 \) mode substantially decreases to give \( \tau = 1.69 \text{ ns at } n = 1 \). Meanwhile, for the \( \nu_9 \) mode,

\[
P_{1D,WKB}(Q) = \exp \left\{ -2 \int_a^b \sqrt{\frac{2\mu}{\hbar}} \left[ V(R_{OH}; Q) - E \right] d(R_{OH}) \right\}. \tag{1}
\]

Here, \( P_{1D,WKB}(Q) \) is the WKB adiabatic tunneling probability as a function of the normal mode displacement (Q), \( \mu \) is the reduced mass in the H atom detachment process, \( R_{OH} \) is the O–H bond length, \( E \) is the zero-point vibrational energy along the O–H bond extension coordinate (\( \nu_{OH}/2 \sim 1790 \text{ cm}^{-1} \)), whereas \( a \) and \( b \) represent the classical bounds of the tunneling barrier. The \( P_{1D,WKB}(Q) \) is calculated for the tunneling through the one-dimensional adiabatic potential energy curve (along the O–H bond extension coordinate) given at the specific normal mode displacement (Q) of the vibrational mode of interest. \( P_{1D,WKB}(Q) \) is then weight averaged according to the probability distribution of the \( S_1 \) wave function \( (\psi_{\nu}^2(Q))^2 \) of the \( i \mathrm{th} \) vibrational mode with the \( n \) quantum number to give the two-dimensional WKB tunneling probability \( P_{WKB} \) as follows:

\[
P_{WKB} = \int P_{1D,WKB}(Q) \cdot \psi^2(Q) dQ. \tag{2}
\]

The adiabatic PEC modulated along Q is rather complicated in nature as manifested in the skewed conical intersection seam coordinate (Fig. 3) due to the strong mode-coupling during the tunneling process. Just for simplicity, only the height of the effective adiabatic tunneling barrier adjusted along Q at the fixed conical intersection configuration has been taken into account in the \( P_{1D,WKB}(Q) \) calculation (see the supplementary material). The \( S_1 \) lifetime at the specific vibronic mode excitation is derived from the equation of \( \tau = (\nu_{OH} \cdot P_{WKB})^{-1} \). The resultant \( S_1 \) lifetimes calculated by the tunneling probability at the excitations of the \( \nu_1 \) or \( \nu_9 \) mode are listed in Table I, giving an extremely satisfactory explanation of the experiment in light of the very simple adiabatic semi-classical model used here. It should be noted that the \( S_1 \) lifetimes calculated at ZPLs of the individual vibrational modes are all different as each \( S_1 \) lifetime is obtained by the weighted average of the ZPL wave function of a specific vibrational mode only. The qualitative trend of the tunneling rate with the vibrational mode excitation should be thus judged from the comparison of the \( S_1 \) lifetime of \( n = 0 \) to that of \( n = 1 \) (or 2) of the identical vibrational mode. For instance, the \( S_1 \) lifetime of 2.14 ns calculated at \( n = 0 \) of the \( \nu_1 \) mode substantially decreases to give \( \tau = 1.69 \text{ ns at } n = 1 \). Meanwhile, for the \( \nu_9 \) mode,

### Table I. Calculated lifetimes (ns) for the H atom tunneling reaction of the \( S_1 \) phenol using extended 2D WKB methods. For the tunneling lifetime calculation at the 16a2 mode excitation, the \( n = 2 \) waveform has been used. Experimental lifetimes are obtained from Ref. 38.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Impeding ZPL</th>
<th>Spectating ZPL</th>
<th>Expediting ZPL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16a2 (374 cm(^{-1}))</td>
<td>6a1 (475 cm(^{-1}))</td>
<td>9a1 (975 cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>121 (783 cm(^{-1}))</td>
<td>11 (935 cm(^{-1}))</td>
<td>7a1 (1273 cm(^{-1}))</td>
</tr>
<tr>
<td>Ground state (( n = 0 ))</td>
<td>2.48</td>
<td>2.04</td>
<td>1.97</td>
</tr>
<tr>
<td>Excited state (( n = 1 ) or 2)</td>
<td>3.93</td>
<td>2.08</td>
<td>2.02</td>
</tr>
<tr>
<td>Experiment</td>
<td>2.27</td>
<td>2.89</td>
<td>2.17</td>
</tr>
</tbody>
</table>

FIG. 3. Nuclear configurations of the \( S_1 \) minimum energy (blue circle) and the \( S_1/S_2 \) conical intersection (red triangle) projected onto the two-dimensional plane of the (a) \( R_{OH} - \nu_1 \) or (b) \( R_{OH} - \nu_9 \) normal mode coordinates.
the $S_1$ lifetime is calculated to be 1.97 or 2.02 ns at $n = 0$ or $n = 1$, respectively. Remarkably, the experimental fact that the tunneling rate increases (remains unchanged) on the $v_1$ ($v_{9a}$) mode excitation is quite well explained. Tunneling rates are also calculated for the excitations of several other Franck–Condon active vibrational modes of $16a^2$, $6a^1$, $12^1$, and $7a^1$. Although the quantitative reproduction of the experiment is formidable especially as the WKB model seems to be intrinsically inappropriate for the quantitative tunneling rate calculation, the mode-specific behavior of the experimental tunneling rate could be qualitatively well explained, Table I. The effect of the $S_1$ vibrational mode on the tunneling rate, regardless of the internal energy, could be classified into the (i) impeding mode ($16a^2$), (ii) spectator mode ($6a^1$, $9a^1$), or (iii) expediting mode ($12^1$, $1^1$, $7a^1$). The theoretical PECs at the configurations of the $S_1$ minimum energy and the $S_1/S_2$ conical intersection show a similar dynamic behavior to that of the $v_1$ ($v_{9a}$) mode for the expediting (spectator) modes (see the supplementary material). The decrease in the tunneling rate on the $16a^2$ mode excitation (374 cm$^{-1}$) is quite noteworthy. Our simple adiabatic model predicts that the tunneling rate is slowed down by $\sim 1.6$ times at the $16a^2$ mode excitation compared with that at ZPL, which is qualitatively consistent with the experiment but quantitatively even larger than the experiment. The adiabatic tunneling barrier height for the reactive flux spread along the $\nu_{16a}$ mode, explaining exactly why the tunneling is impeded at the $16a^2$ mode excitation.

According to our previous report, the energy disposal dynamics is also strongly influenced by the nature of the $S_1$ vibronic mode excitation. Namely, the $H$ fragment translational energy distribution shows a substantial shift to the higher energy region compared with that at ZPL when the $S_1$ vibronic mode of $12$, $1$, or $7a$ (belonging to the expediting mode category) is excited. This indicates that the vibrational modes expediting the tunneling process may also accelerate the fragment velocity along the $O$–$H$ bond extension coordinate. As the $\pi\sigma^*$ state correlates with the product channels by crossing the $S_0$ potential in the late stage of dynamics, the translational energy distribution is governed by the topography of the repulsive potential energy surface. Figure 4 clearly shows that the PECs obtained along the $v_1$ mode displacement on the $\pi\sigma^*$ surface are substantially shifted from that on the $S_1$ minimum by $\sim 0.18$ a.u., showing that the $v_1$ mode is much more strongly coupled to the $H$ atom tunneling coordinate as the reaction proceeds further. Equivalently, the vibrational internal energy given by the $v_1$ mode excitation is partitioned into the coupled reaction coordinate to exhibit the relatively larger translational energies of fragments compared with the case at ZPL. The shift of the larger translational energy distribution of the fragments at the $1$, $12$, or $7a$ normal modes.

![FIG. 4](https://example.com/figure4.png) (Upper) Potential energy curves calculated along the $1$ (left) or $9a$ (right) normal mode displacement coordinate at the optimized geometries at the $S_1$ minimum (EQ, open blue circles), the outer classical bound of the tunneling barrier ($R_{OH} = 1.7$ Å, red inverted triangles), or the second $S_0/S_2$ conical intersection ($R_{OH} = 2.2$ Å, orange diamonds). The calculated data points are smoothly fit using the quartic polynomial functions (lines). (Lower) The wave function amplitude of the excited vibrational state ($n = 1$) obtained at the $S_1$ equilibrium geometry for $1$ (left) or $9a$ (right) mode.
mode excitation could be then rationalized by the skewed $S_1/S_2$ conical intersection on the two-dimensional coordinates. The experimental finding that the translational energy distribution remains unchanged at the 6a or 9a mode excitation (from that found at the ZPL) could be also explained by the absence of the coupling to the reaction coordinate at the conical intersection (see supplementary material). It is quite notable that the 6a or 9a mode excitation of the $S_1$ phenol seems to be conserved in the internal energy distribution of the final fragment of $C_6H_5O^− (\lambda)$).\cite{Xie}\cite{Xie} This strongly suggests that 6a and 9a belong to the spectator modes, which is quite consistent with the conclusion from a recent theoretical study by Xie et al.\cite{Xie} that the $v_{6a}$ mode excitation of the $S_1$ phenol is not responsible for the vibrational excitation of the final photoproducts.\cite{Xie} It will be interesting to see how the internal energy of the $C_6H_5O^-$ ($\lambda$) would be modulated when the strongly coupled modes (to the tunneling coordinate) of 1, 12, or 7a is excited in $S_1$. Further experimental investigation in this direction would be highly desirable. The larger translational energy of the photofragment that is available. The larger translational energy of the photofragment that is equivalent to the faster wave packet movement on the repulsive $\pi^\ast$ state may lead to the increase of the nonadiabatic transition probability at the $S_0/S_2$ conical intersection according to the semi-classical Landau–Zener model, $P_{NT} (v) = \exp (-\xi/v)$, where $\xi$ represents the off-diagonal coupling matrix elements in the diabatic representations of two crossing curves, whereas $v$ is the velocity of wave packet passing through the conical intersection region.\cite{Landau-Zener} The branching ratio into the high/low transitional energy distributions that is supposed to be proportional to the nonadiabatic transition probability has been estimated to be $\sim 2.48, \sim 2.36$, or $\sim 2.31$ at the excitation of the 12, 1, or 7a modes, respectively.\cite{Kim} This is significantly larger than the ratio of $\sim 1.94, \sim 1.60$, or $\sim 1.80$, estimated at the ZPL, 6a, or 9a modes, respectively. Quite impressively, this is quite consistent with the mode-dependent behavior of the tunneling rate (vide supra).

CONCLUSIONS

The remarkable role of the normal modes on the seam coordinates has been manifested in the H atom tunneling dynamics of the $S_1$ phenol by examining the local topography of conical intersection on the reduced two-dimensional PESs. The mode-specific dynamic output of the tunneling rate, the translational energy distribution, or the nonadiabatic transition probability shows a nice correlation with the mode-dependent configurational shift of the PES at different positions along the O–H bond extension coordinate (Fig. S4 of the supplementary material). The strong correlations between the configurational shifts and the dynamic outputs indicate that the topography of the PES along the particular vibrational mode dictates the overall tunneling dynamics in rate, energy disposal, and nonadiabatic transitions. Through our analysis of the mode effect of the $S_1$ phenol dynamics, it is confirmed here that the conical intersection configurations extended along the $(3N – 8)$ seam coordinates should play the pivotal role in dictating the nonadiabatic dynamics of the reactive flux in the proximity of the conical intersection.

SUPPLEMENTARY MATERIAL

See the supplementary material for calculation details, rigid-body potential energy curves of phenol along the several $S_1$ normal mode coordinates, summary on the vibrational mode effects in the nonadiabatic tunneling dynamics of phenol, and schematic PESs illustrating the vibrational mode effect in the product translational energy distribution.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Junggil Kim: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). Kyung Chul Woo: Data curation (equal); Formal analysis (equal); Investigation (equal). Sang Kyu Kim: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


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