

Insights into the Mechanism of Nonadiabatic Photodissociation from Product Vibrational Distributions. The Remarkable Case of Phenol

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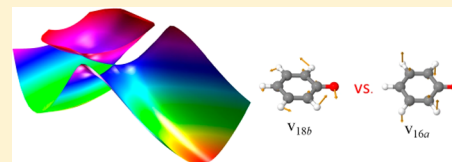
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Supporting Information

ABSTRACT: The fate of a photoexcited molecule is often strongly influenced by electronic degeneracies, such as conical intersections, which break the Born–Oppenheimer separation of electronic and nuclear motion. Detailed information concerning internal energy redistribution in a nonadiabatic process can be extracted from the product state distribution of a photofragment in photodissociation. Here, we focus on the nonadiabatic photodissociation of phenol and discuss the internal excitation of the phenoxy radical using both symmetry analysis and wave packet dynamics. It is shown that unique and general selection rules exist, which can be attributed to the geometric phase in the adiabatic representation. Further, our results provide a reinterpretation of the experimental data, shedding light on the impact of conical intersections on the product state distribution.



The photochemistry of cyclic aromatic molecules such as phenols, pyrroles, azoles, and indoles have attracted much recent attention because of their importance in the photostability of biologically relevant chromophores (e.g., nucleobases in DNAs and amino acids in proteins).^{1–3} Despite strong absorption bands in the UV region, these molecules have small fluorescence quantum yields, suggesting efficient nonradiative decay channels. The ultrafast internal conversion (IC) is thought to offer an effective protection mechanism for the building blocks of life.^{4,5} It is now well established that such radiationless channels are facilitated by nonadiabatic transitions through electronic degeneracies such as conical intersections (CIs), a double-cone shaped degeneracy formed between adiabatic electronic states.^{6–8} As a result, detailed knowledge of nonadiabatic dynamics is essential to gain a complete understanding of these important photoprocesses.^{5,9–13}

Among such molecules, phenol is perhaps the most extensively studied.¹⁴ Electronic structure calculations by Sobolewski and Domcke revealed that its first absorption band near 275 nm¹⁵ stems from a ${}^1\pi\pi^*(S_1) \leftarrow {}^1\pi\pi(S_0)$ excitation.^{16,17} Near the Franck–Condon region, as shown in Figure 1, the bright ${}^1\pi\pi^*$ state forms a CI (CI_1) seam with a dark and repulsive ${}^1\pi\sigma^*$ state, which correlates diabatically to H and the phenoxy radical in its ground electronic state ($C_6H_5O(\tilde{X}^2B_1)$). At large O–H distances, the ${}^1\pi\sigma^*$ state forms another CI (CI_2) seam with the ground ${}^1\pi\pi$ state.

This nonadiabatic dissociation mechanism was confirmed by experiments.^{18–32} In particular, the H fragment has been detected upon photodissociation^{18,21} and real-time measurements corroborated the tunneling nature of the dissociation.^{24,26,29,30} More details concerning the dissociation dynamics were revealed by the kinetic energy release (KER) of the H fragment, which in high resolution provides information on the extent of internal excitation in the phenoxy cofragment at a given photon wavelength. Using the H atom Rydberg tagging technique, the KER has been measured by Ashfold and co-workers at several photon wavelengths via two ${}^1\pi\pi^*$ (S_1 and S_3) states.^{19,20,22,27} There are broad features in the KER, attributable to statistical dissociation. This is expected after IC to the ground electronic state dominated by a deep well. However, there are also pronounced structures, particularly for fast H fragments corresponding to the H + $C_6H_5O(\tilde{X}^2B_1)$ channel, suggesting a nonstatistical internal state distribution in the phenoxy product from a direct nonadiabatic channel.^{19,20,22} Such distinct product state distributions offer unique insights into the nonadiabatic dissociation dynamics, which is the topic of the current work.

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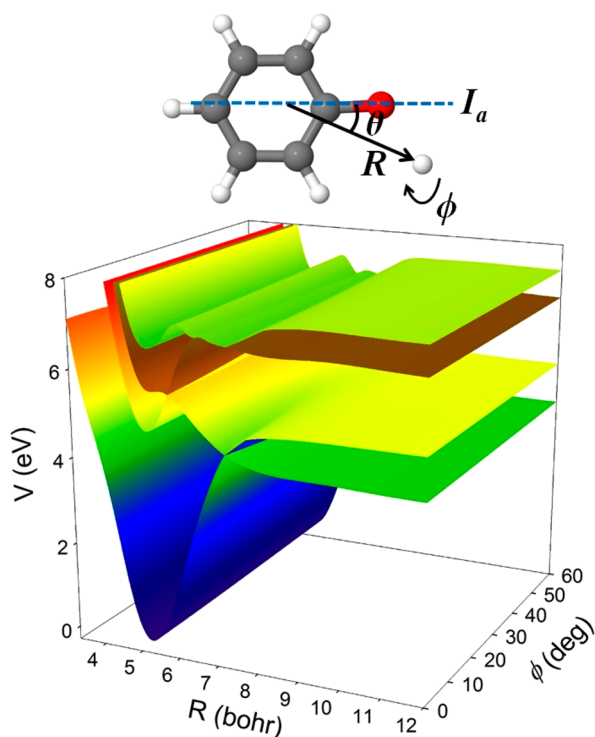


Figure 1. Adiabatic PESs for the phenol along the R and ϕ coordinates. The three coordinates (R , θ , ϕ) used in the 4D models are shown in the inset.

The structure in the H atom KER is dominated by a progression with an energy spacing of approximately $300\text{--}500\text{ cm}^{-1}$, and this progression persists in a range of excitation frequencies. It is thus quite desirable to identify the excited vibrational mode(s) of phenoxyl as they carry valuable information about the nonadiabatic dynamics. It was argued that because of the different electronic symmetries between the bright photoexcited state (${}^1\pi\pi^*$ or S_1), which has A' symmetry (C_s point group), and the dark dissociative state (${}^1\pi\sigma^*$ or S_2), which has A'' symmetry, the allowed vibrational modes for the $C_6H_5O(\tilde{X}^2B_1)$ fragment, which also has A'' symmetry, must have a'' symmetry.^{19,20,22} This notion was reinforced by the fact that the coupling mode of CI_1 is of a'' symmetry,¹⁷ which helped to lead to the conclusion that nonadiabatic transitions near CI_1 must be mediated by a vibrational mode of phenol with a'' symmetry. When these restrictions are taken into consideration, the observed progression was assigned primarily to the ν_{16a} mode, which has a'' symmetry and a frequency of 372.9 cm^{-1} , along with some excitation in the ν_{18b} mode.^{19,20,22} Furthermore, it was argued that only the odd quanta of this a'' vibrational mode (ν_{16a}) are allowed and that this propensity is a signature of the geometric phase (GP) effect associated with CI_1 .²⁵ This assignment has since been fortified by several later studies of thiophenol²² and substituted (thio)phenols.^{33–35}

In the meantime, the accumulated experimental data have stimulated many theoretical studies of both electronic structure and dissociation dynamics for the photodissociation of phenol.^{36–51} Our recent advances in this direction have been made possible by the development of full-dimensional coupled diabatic potential energy matrices (PEMs) for this system.^{12,52} One such global PEM involving the three lowest coupled electronic states was constructed in full 33 dimensions for this system by Truhlar and co-workers.^{41,42} Yarkony and co-

workers also reported four-state and two-state full-dimensional PEMs using quasi-diabatic representations constructed from adiabatic energies, energy gradients, and derivative couplings.^{43,45,46,48} The availability of these full-dimensional PEMs has enabled detailed calculations of nonadiabatic dynamics.^{44,47,49–51} Unfortunately, none of these dynamical studies has so far produced the internal state distribution of the phenoxyl product, due apparently to the large (30) number of vibrational modes in this radical. As a result, the assignment of the experimental H atom KER^{19,20,22} remains an open question.

We first consider the symmetry of wave functions in the presence of the CIs. Following Ashfold et al.,^{19,20,22} we work with the C_s point group symmetry. As pointed out by Dixon et al.,³⁸ because two equivalent C_s structures interconvert, a more rigorous discussion should be based on the G_4 subgroup of the complete nuclear permutation and inversion (CNPI) group,⁵³ which is isomorphic to the C_{2v} point group. This discussion can be found in the [Supporting Information](#).

A transition from the ${}^1\pi\pi^*$ diabat (A') in the Franck–Condon region to the repulsive ${}^1\pi\sigma^*$ diabat (A'') is accompanied by a change of electronic symmetry along out-of-plane coordinates. It follows that a nuclear wave function on a given adiabatic state changes its symmetry with respect to planar geometry as it passes through CI_1 .⁴⁷ On the lower adiabatic state (S_1) associated with CI_1 , for example, a nodeless nuclear wave function in the Franck–Condon region, which has a' symmetry, acquires a node in the dissociation channel outside the CI and thus becomes the a'' symmetry.¹³ This change of the out-of-plane symmetry in the lower adiabatic state is a manifestation of the GP around the CI,^{49,54} namely the topological phase acquired by the adiabatic electronic wave function along a path encircling the CI.^{55,56} Accordingly, the node in the adiabatic nuclear wave function can be thought of as a result of destructive interference between two tunneling trajectories on two paths along two sides of the CI.^{54,57–60} While their dynamical phases are identical, they acquire GPs that are completely out of phase, leading to destructive interference that is responsible for the retardation of tunneling lifetime in phenol photodissociation on the S_1 state, as discussed in our recent work.^{47,49,54}

Although it forms a CI with the ground ${}^1\pi\pi$ state, the diabatic ${}^1\pi\sigma^*$ state on which the subsequent dissociation to the $C_6H_5O(\tilde{X}^2B_1)$ channel takes place maintains the same A'' symmetry. As a result, if the initial nuclear wave function on the ${}^1\pi\pi^*$ state is of a' symmetry, such as the ground rovibrational state, the nuclear wave function in the $C_6H_5O(\tilde{X}^2B_1)$ asymptote should have a'' symmetry, as correctly pointed out by Ashfold and co-workers.^{19,20,22} Alternatively, if the initial nuclear wave function on the ${}^1\pi\pi^*$ state is of a'' symmetry, the nuclear wave function in the $C_6H_5O(\tilde{X}^2B_1)$ asymptote should have a' symmetry. Ashfold and co-workers argued further that an a'' vibrational mode is required to mediate nonadiabatic transitions through CI_1 .^{19,20,22} However, this argument was later disputed by Domcke and co-workers because the out-of-plane OH torsional mode also has a'' symmetry and this disappearing mode is almost certainly involved in mediating nonadiabatic transitions in phenol dissociation.³⁶ This latter conclusion was also confirmed by our own work.⁴⁷

A key observation of the present work is the realization that the a'' symmetry in the nuclear wave function in the $C_6H_5O(\tilde{X}^2B_1)$ channel needs not be realized by the vibrational

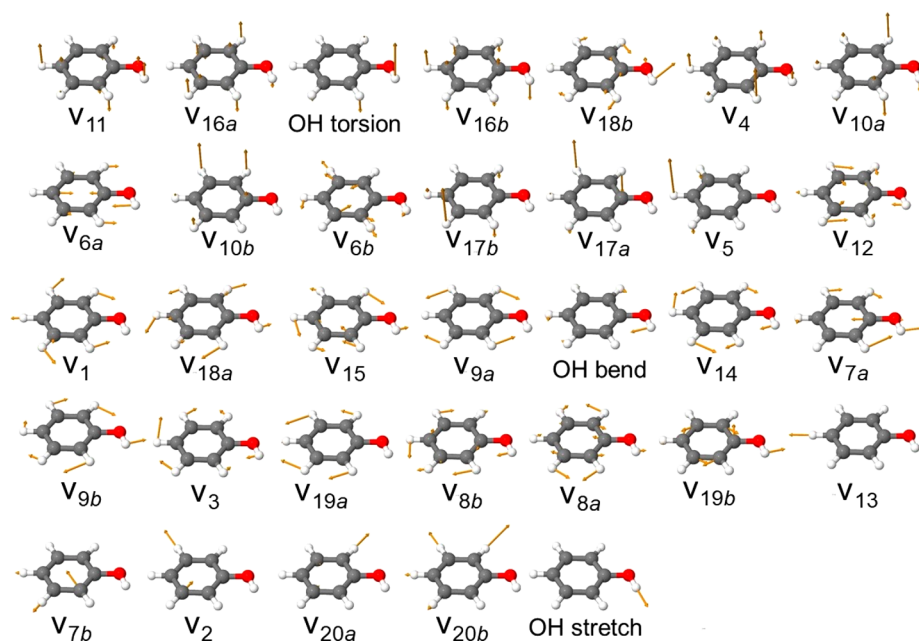


Figure 2. Mass-weighted normal mode vectors of the 33 vibrational modes of $C_6H_5OH(S_0)$ using Wilson's nomenclature.

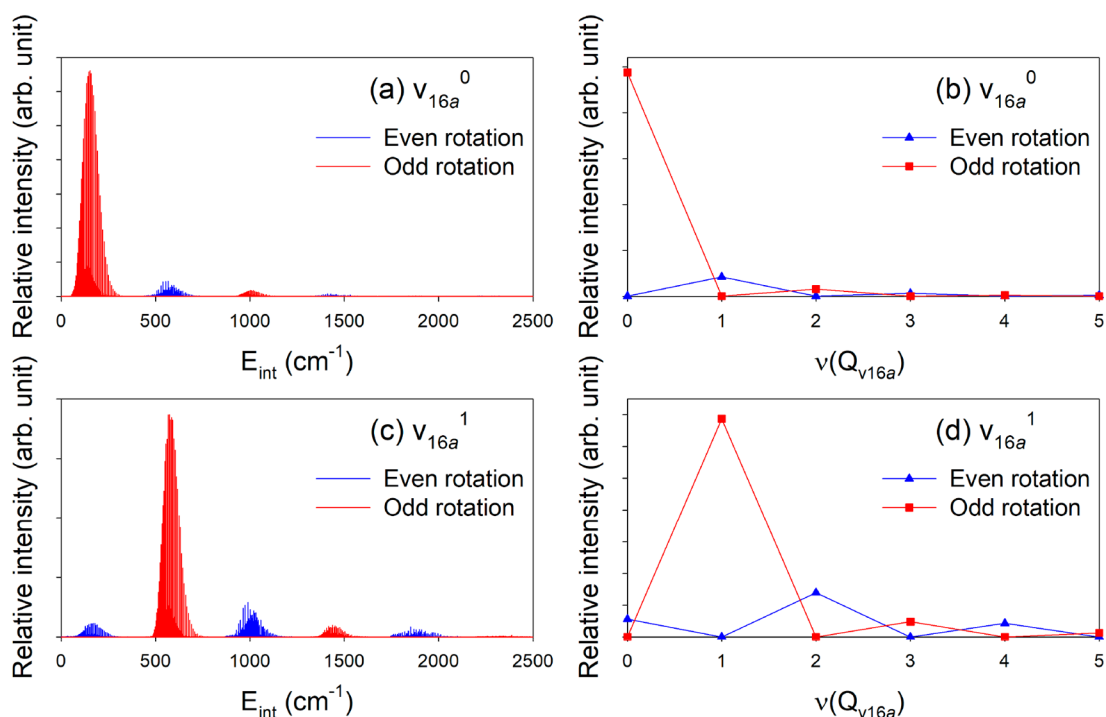


Figure 3. Product ro-vibrational and vibrational state distributions for $C_6H_5O(\tilde{X}^2B_1)$ upon photoexcitation to the $v_{16a} = 0$ and 1 states of the S_1 state obtained with the 4D model with $Q = v_{16a}$.

wave function alone, as the *rotational* wave function can have either a' or a'' symmetries. It follows that the overall nuclear wave function of a'' symmetry in the $C_6H_5O(\tilde{X}^2B_1)$ asymptote could be the consequence of either $a'_{\text{vib}} \otimes a''_{\text{rot}}$ or $a''_{\text{vib}} \otimes a'_{\text{rot}}$. Consequently, the restriction of the odd a'' vibrational quanta in the phenoxy fragment in the original symmetry consideration is unnecessary. This conclusion is illustrated by wave packet calculations detailed below.

In this work, we examine the dissociation dynamics using reduced-dimensional quantum dynamics models based on the Zhu-Yarkony PEM.^{45,46} This PEM has been used in our

previous reduced-dimensional quantum dynamics studies, in which the calculated tunneling lifetime was found to agree with experiment quite well.^{47,51} Here, we focus on the product state distributions.

Multiple four-dimensional (4D) models are used here, and all include the three disappearing coordinates (R , θ , ϕ) in phenol photodissociation as shown in Figure 1. Here, R is the distance between the C_6H_5O center of mass and the dissociating H atom, θ the angle between R and the inertial axis I_a of C_6H_5O along its C_{2v} axis, and ϕ the out-of-plane angle of the H atom. The inclusion of the R and ϕ DOFs is essential

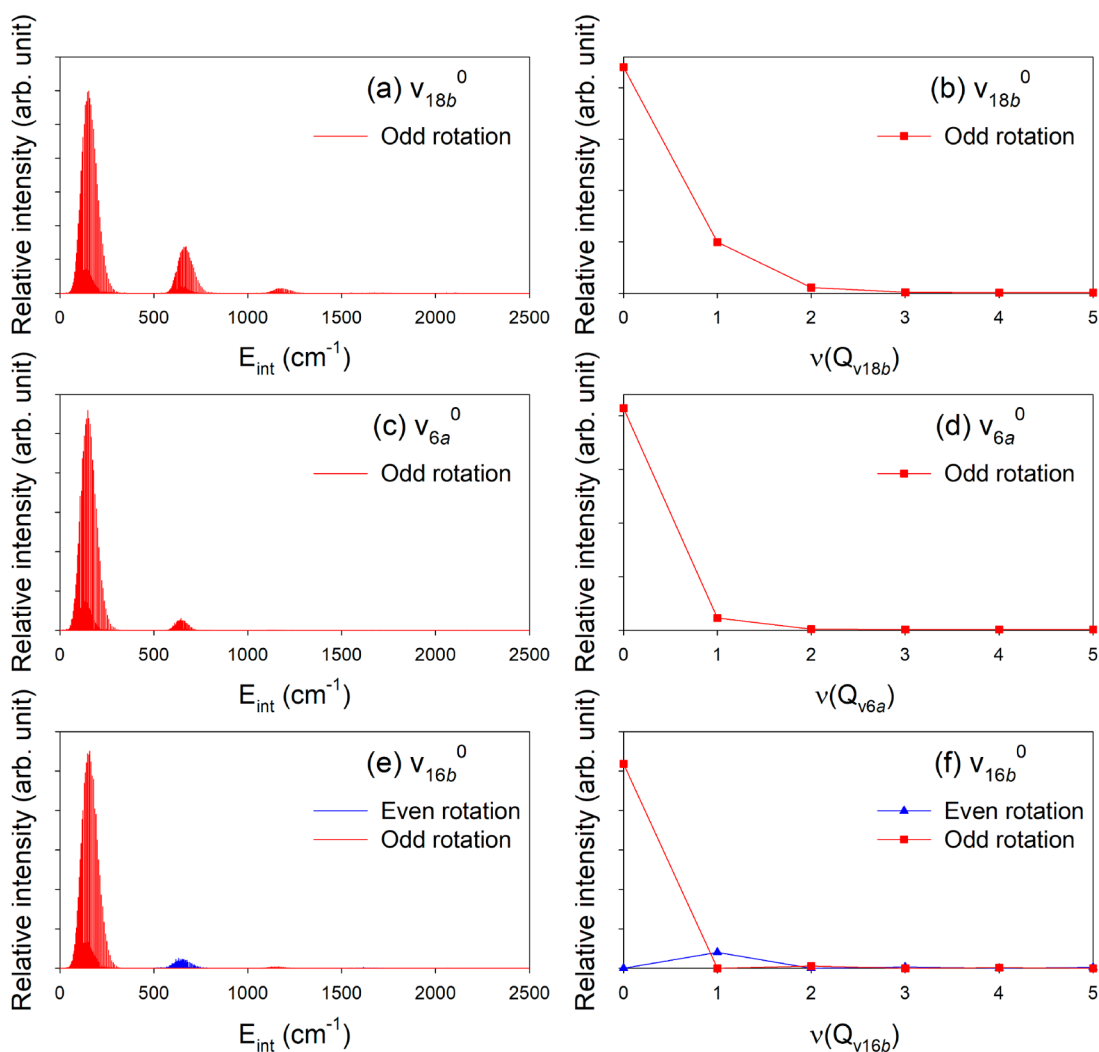


Figure 4. Product ro-vibrational and vibrational state distributions for $C_6H_5O(\tilde{X}^2B_1)$ obtained using the 4D models with $Q = \nu_{18b}$, ν_{6a} and ν_{16b} .

because they are approximately the **g** and **h** vectors spanning the branching space of CI_1 and thus are intimately involved in the nonadiabatic dynamics.^{36,61} Each 4D model includes one additional normal mode (Q) of the phenyl ring, aiming at a better understanding of the involvement of this mode in the dissociation dynamics. These models provide a reasonably faithful characterization of the dissociation dynamics, because photodissociation is largely a process involving only a small subset of modes while other modes are almost spectators. This is borne out by evidence provided below. We stress that the symmetry analysis provided above is rigorous and not affected by the neglect of modes in our reduced-dimensional models. The details of the quantum dynamical calculations can be found in the [Supporting Information](#).

There are 33 vibrational modes in phenol, and these normal modes on the $S_0(1\pi\pi)$ state are displayed in [Figure 2](#), using Wilson's nomenclature.⁶² Apart from the OH stretching, COH bending, and CCOH torsional modes, the same labels can be used for the vibrational modes of the phenoxyl radical. Vibrational frequencies and rotational constants of phenoxyl in both the ground and first excited states have been computed using the 4D models, and the comparison with literature values^{20,27,63–66} provides strong support for the validity of this reduced-dimensional approach, as discussed in detail in the [Supporting Information](#).

The nonadiabatic dynamics calculations were performed with 4D models in which the normal mode (Q) was chosen to be one of the following modes: ν_{6a} , ν_{16a} , ν_{16b} , or ν_{18b} . The main reason for choosing these modes is that their frequencies are close to 400 cm^{-1} , thus potentially responsible for the experimentally observed fast KER features.^{19,20,22} Among these four representatives, ν_{16a} and ν_{16b} are out-of-plane modes (a''), while the others are in-plane modes (a') (see [Table S2](#)). In addition, the excited vibrational state with $\nu_{OH} = 1$ was chosen as the initial state in the photodissociation process, because the lifetime of the ground vibronic state of $S_1(1\pi\pi^*)$ state is too long ($\sim 2\text{ ns}$)^{15,28,29,32} to be simulated by wave packet propagation. It is important to stress that the excitation in the OH mode is not expected to change the symmetry properties, because it is orthogonal to the **h** vectors.

First, we examine the 4D model with the ν_{16a} mode included. For an initial state that has no excitation in this mode, the internal energy distribution of the phenoxyl fragment and its vibrational state distribution summed over all the rotational states are shown in panels (a) and (b) of [Figure 3](#), respectively. It is clear from the figures that both odd and even vibrational quanta are allowed, but they are accompanied by rotational states with even and odd parities, respectively. This is a direct demonstration of the GP effect in the product channel wave function, as we discussed above.

However, our results do not observe the “odd-quantum selection rule” proposed by Ashfold et al.,^{19,20,22} who did not include the rotational symmetry of the product in their consideration. Furthermore, the vibrational distribution is dominated by the ground vibrational state population. This is again in sharp contrast with the previous assignment in which the ground vibrational state was assumed to have no population.^{19,20,22} The domination of the ground vibrational state in the product state distribution suggests that this mode is largely a spectator during the nonadiabatic photodissociation of phenol. To further confirm its spectator nature, the product state distribution is investigated with an initial wave packet with one quantum in the ν_{16a} mode of phenol. The results in Figures 3(c) and 3(d) clearly show that the initial excitation in this parent mode is largely preserved in the phenoxy fragment, confirming its spectator nature. The results in Figure 3 present convincing evidence that the ν_{16a} mode is unlikely to be responsible for the vibrational progression observed in the experimental KER, because the populations of the vibrationally excited states are too low, despite the frequency match.

To explore alternative possibilities, we have performed 4D calculations with the other three possible candidates, and the results are shown in Figure 4. For the two in-plane modes (ν_{18b} and ν_{6a}), all vibrational states are accompanied by rotational states with the odd parity, which renders the overall a'' nuclear symmetry. For the other out-of-plane mode (ν_{16b}), the even and odd vibrational states are again accompanied by rotational states with odd and even parities, respectively, in analogy to the ν_{16a} mode shown in Figure 3. In all three cases, the vibrational state distribution decays monotonically with the corresponding vibrational quantum, but the ν_{18b} mode has the most vibrational excitation and is the most likely candidate for the vibrational progression in the experimental fast H atom KER. This is readily understandable mechanically because this in-plane CO wagging mode is expected to experience a strong recoil due to the departing H atom.²²

In Figure 5, the product internal energy distributions of the 4D models with the four normal modes are compared with the experimental distribution derived from the KER at 275.11 nm²² with respect to the zero-point energy of the product ($E_{\text{int}} = 0$). It should be noted that the second and third peaks in each calculated distribution were shifted by the small energy difference between the measured and calculated vibrational frequencies, in order to mitigate the overestimation of the vibrational frequency in our 4D models. The agreement is quite remarkable, particularly for the first two peaks. The theory–experiment comparison for higher peaks (especially larger than ~ 1000 cm⁻¹) is beyond the scope of this work, but it is conceivable that other higher-frequency modes or combination bands might be involved. On the basis of these results, we tentatively assign the vibrational progression in the fast H atom KER at 275.11 nm observed in the experiment of Ashfold and co-workers^{19,20,22} to be primarily due to the in-plane ν_{18b} mode (which was also assigned to be excited in previous analyses^{19,20,22}), with smaller contributions from other modes. The origin of the vibrational excitation in this and other modes is discussed using a normal coordinate displacement model⁶⁷ in the Supporting Information.

A consequence of this new assignment is a revised dissociation energy of the ground electronic state of phenol. Different from the previous assignment of Ashfold et al.,^{19,20,22} which placed the band origin 225 cm⁻¹ below the first feature of the vibrational progression in KER because of the “odd

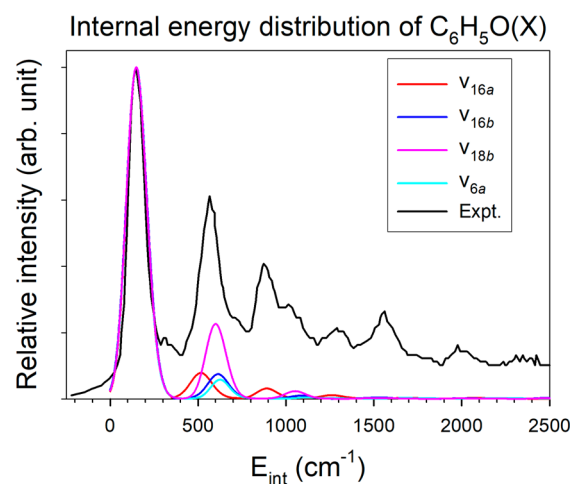


Figure 5. Comparison of the calculated phenoxy internal energy distribution with the experimental data measured at 275.11 nm.²² The latter was chosen to match the first peaks of the calculated and experimental results. For all higher peaks, the calculated ones were shifted lower by $\nu \cdot \Delta$, in which Δ is the vibrational frequency deviation of our 4D results from available experimental⁶³ (ν_{18b} , ν_{6a} , and ν_{16b}) or calculated²⁰ (ν_{16a}) values for each mode, shown in Table S4. The Δ values are -60.6 , -58.8 , -31.7 , and -15.7 cm⁻¹ for ν_{18b} , ν_{16a} , ν_{16b} , and ν_{6a} , respectively.

quantum rule”, we assign the first feature as the band origin. In addition, our calculations indicate significant rotational excitation in the phenoxy product, which was ignored in the assignment of Ashfold et al.^{19,20,22} Indeed, the peak corresponding to the ground vibrational state of $C_6H_5O(\tilde{X}^2B_1)$ contains ~ 153 cm⁻¹ of rotational energy, using the 4D model with the ν_{18b} mode. The most populated rotational state for $\nu = 0$ is the odd symmetry one with $J = 48$ and $K_c = 47$ (odd $J + K_c$) of $C_6H_5O(\tilde{X}^2B_1)$. The propensity for $K_c \approx J$ is due to the torque exerted by the recoiling H, which leads mostly to the rotational excitation of phenoxy along the I_c axis. Despite the significant rotational excitation, the rotational state distribution is relatively narrow (~ 90 cm⁻¹ fwhm), consistent with the 100 cm⁻¹ line width in the high-resolution KER distribution.²⁰ When these factors are taken into consideration, the corresponding D_0 is calculated to be $30\,087 \pm 40$ cm⁻¹, 72 cm⁻¹ larger than the previous value of $30\,015 \pm 40$ cm⁻¹.^{19,20,22} We note in passing that the previous assignment of Ashfold et al. was also motivated by a slight inconsistency between the extrapolated D_0 values from the vibrational features in the $\lambda < 248$ nm and $\lambda > 248$ nm regions.^{19,20,22} Because the origin of the photoabsorption for $\lambda < 248$ nm involves a higher $\pi\pi^*$ state, our results reported here do not help to resolve this inconsistency.

It has long been recognized that CIs play a vital role in nonadiabatic dynamics in photochemistry. However, our understanding of nonadiabatic dynamics around a CI is still incomplete, especially concerning the role of the GP. It has been a long-standing goal in photochemistry to uncover signatures of the GP, and there have been extensive discussions on this topic.⁶¹ In photodissociation, the richest information concerning dissociation dynamics is contained in the product state distribution. In this work, we focus on such signatures in the photodissociation of phenol, which has served as a key prototype in understanding nonadiabatic dynamics in photochemistry. Our symmetry-based analysis and reduced-dimensional quantum dynamics calculations on a first-principles-

based diabatic PEM conclude that a previously proposed selection rule based on electronic and vibrational symmetries is flawed, owing to the neglect of the rotational symmetry of the phenoxyl product. The GP effect manifests in the total symmetry of the wave function, represented by a direct product of electronic, vibrational, and rotational symmetries. The neglect of the product rotational symmetry thus presents an incomplete picture of the dynamics. As such, the discussion presented in this work offers a general guideline for product state distributions in this and other related systems.

Our calculations based on an accurate diabatic PEM suggest that the ν_{16a} mode of the phenoxyl group is unlikely to be responsible for the vibrational progression observed in the H atom KER, as it is essentially a spectator mode. Instead, our results argue that the vibrational excitation of phenoxyl is most likely in the ν_{18b} mode, because of a mechanical effect due to the recoil of the H fragment. Furthermore, relaxing the restriction of odd quantum number vibrational populations means that the band origin including vibrational structure should be taken as the vibrational ground state of the phenoxyl product. This new realization, coupled with the inclusion of rotational excitation of the product, leads to a revised D_0 value of $30\,087 \pm 40 \text{ cm}^{-1}$. We hope these new insights will motivate future experiments and more elaborate theoretical treatments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.9b03407>.

Details of the analysis and calculations; additional results (PDF)

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Notes

The authors declare no competing financial interest.

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