

Photodissociation Dynamics of H₂S via the 3¹A' State: Dominance of Dual Intersection-Induced Barriers

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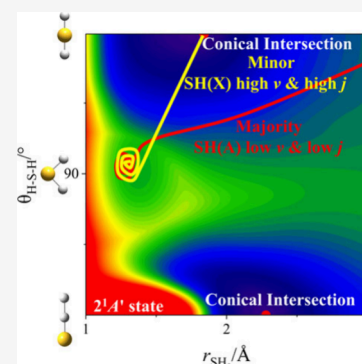


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ABSTRACT: Hydrogen sulfide (H₂S), a major sulfur carrier in the interstellar medium, undergoes ultraviolet photodissociation that shapes interstellar sulfur chemistry and sulfur isotope fractionation. Here we construct a four-state diabatic potential energy matrix for the lowest four ¹A' states of H₂S using high-level *ab initio* data and a neural-network-based diabaticization scheme. Quantum wave packet dynamics on the 3¹A' state reproduce the main experimental features of the H + SH(X²Π/A²Σ⁺) internal energy distributions at 143.15 nm, with minor discrepancies likely due to the unaccounted contributions of ¹A'' states. Trajectory surface-hopping simulations show that H₂S undergoes transient trapping in a basin formed by dual intersection-induced barriers on the 2¹A' surface. This dual-barrier topology restricts dissociation to a narrow escape pathway along the bond-angle coordinate, promoting SH(A²Σ⁺) formation. The results reveal a new mechanism in which dual intersection-induced barriers govern product branching in high-lying electronic states.



Since its first detection in the Orion KL source in the 1970s,¹ hydrogen sulfide (H₂S) has been ubiquitously observed in cold, dense regions of the interstellar medium, including star-forming regions, prestellar cores, and protoplanetary disks. These discoveries have drawn broad interdisciplinary interest from both astronomers^{2–8} and chemists.^{9–26} As one of the most abundant sulfur-bearing molecules in the universe, H₂S serves as both a primary sulfur reservoir in space and a precursor for complex organic sulfur compounds.^{27,28} A distinctive feature of H₂S is its complex electronic structure and diverse photochemical pathways.²⁶ Under vacuum ultraviolet (VUV) irradiation, it can produce H(²S), H₂, S(¹D/³P), and SH(X²Π/A²Σ⁺) fragments undergoing intricate photodissociation processes.^{25,26} Notably, the electronically excited SH(A²Σ⁺) radical undergoes rapid predissociation, yielding hydrogen and sulfur atoms on the nanosecond time scale or faster.²⁹ These photofragments actively participate in both gas-phase and surface-mediated chemical reactions within the interstellar medium,³⁰ thereby driving the formation of a diverse array of sulfur-containing species.^{27,28,30,31} In parallel, isotope geochemists have identified mass-independent fractionation of sulfur isotopes (S-MIF) in meteorites and other natural archives preserving records of solar system evolution,³² with S-MIF variations among meteorite classes reflect the different photochemical conditions of their formation environments.³² Laboratory experiments by Chakraborty et al.³² showed that the photodissociation of H₂S under VUV irradiation produces wavelength-dependent S-MIF, meteorites subsequently incorporate these S-MIF—particularly SH(A²Σ⁺) and S(³P)—thereby enabling the

reconstruction of early solar system processes. However, despite this importance, the mechanistic origin of S-MIF in H₂S photodissociation and the product branching under VUV irradiation remains poorly understood, motivating a detailed investigation of its underlying dynamics.

VUV excitation promotes valence electrons into Rydberg orbitals, creating a dense network of strongly coupled states linked by conical intersections (CIs), avoided crossings (AVCs), and other nonadiabatic interactions.³³ Rydberg-state photodissociation dynamics have been extensively studied experimentally for molecules such as H₂O,^{34–40} N₂O,^{41–45} H₂S,^{10,11,15,22,25,26,46} CO₂^{47–49} and OCS.^{50–54} These molecules undergo multiple nonadiabatic transitions, leading to diverse product channels.^{26,36,42,49} Among them, H₂O serves as a prototype system: its photodissociation is dominated by the OH(X²Π) channel, where molecules excited to high-lying ¹A' Rydberg states ($\tilde{D}$,⁵⁵ $\tilde{E}$,⁵⁶ and $\tilde{F}$ ⁵⁷) converge on a common intermediate state $\tilde{B}$. This state accesses the CIs between the $\tilde{B}$ and $\tilde{X}$ surfaces without a barrier, followed by efficient nonadiabatic transitions, forming predominantly the ground-state OH(X²Π) fragment.^{35,55,56,58} In H₂S, the 2¹A' state and 1¹A' state are coupled by conical intersections at similar linear

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geometries as those connecting $\tilde{B}$ and $\tilde{X}$ states in H_2O . However, despite the similar linear CIs between H_2S and H_2O , previous experiments show that H_2S photodissociation conversely yields a large fraction of excited-state $\text{SH}(\text{A}^2\Sigma^+)$ fragments, with only minor ground-state $\text{SH}(\text{X}^2\Pi)$.^{15,26} Thus, although H_2S possesses $2^1\text{A}'$ - $1^1\text{A}'$ CIs at similar linear geometries, these intersections are not dynamically important and do not govern the dominant dissociation pathway. The mechanism responsible for this contrasting behavior remains unclear.

In contrast to a wealth of experimental data,^{10,11,13–20,22,25,26,46,59} theoretical studies on the high-lying electronic states of H_2S are comparatively limited. Earlier works on the $1^1\text{A}'$ states were limited to potential energy curves^{60,61} and reduced-dimensional PESs.^{15,22,62} Cook et al. developed two-dimensional adiabatic PESs involving the $1^1\text{A}'$ and $2^1\text{A}'$ states and performed classical trajectory calculations on the $2^1\text{A}'$ state PES.²² More recently, the adiabatic PESs for the ten lowest-lying singlet states of this system have been developed, providing a more comprehensive view of H_2S photofragmentation and highlighting the crucial role of nonadiabatic effects in its photochemistry.²⁶ However, dynamics simulations have so far been limited to the first absorption band of H_2S , corresponding to the lowest two $1^1\text{A}''$ states.^{63–66} For higher-lying states, accurate electronic structure calculations are particularly challenging due to the Rydberg-state character, which demands a carefully chosen active space and extensive basis sets. Another major challenge lies in diabatizing multiple interacting states, especially when the energy spacing is small and several intersections coexist among densely packed Rydberg states.

In this work, we constructed a four-state diabatic potential energy matrix (DPEM) for the lowest four $1^1\text{A}'$ states, explicitly incorporating their couplings associated with multiple CIs and AVC. Quantum dynamics and trajectory surface-hopping (TSH) simulations were then performed to investigate the photodissociation dynamics of H_2S at 143.15 nm. The results reveal that the dynamics are strongly governed by a unique topology of the $2^1\text{A}'$ PES which transiently traps the system in a potential basin by two nearby intersection-induced (with the upper $3^1\text{A}'$ state) barriers. Escape can only occur through a narrow range of bond angles, steering a large proportion of trajectories away from the linear $2^1\text{A}'/1^1\text{A}'$ CIs. Consequently, $\text{SH}(\text{A}^2\Sigma^+)$ emerges as the dominant product, with only minor $\text{SH}(\text{X}^2\Pi)$ products. Overall, our study uncovers a novel mechanism in which dual intersection-induced barriers create transient trapping that governs product branching. Importantly, to address the challenges of diabatization, we modified the approach of Xie and co-workers,⁶⁷ originally inspired by the diabatization-by-ansatz approach,^{68,69} by incorporating electronic properties to ensure a consistent description of the CI topology.

Accurate description of the high-lying Rydberg states of H_2S requires a balance between large active spaces and computational feasibility. In this work, we employed state-averaged complete active space self-consistent field (SA-CASSCF)^{70,71} and internally contracted multireference configuration interaction (ic-MRCI)^{72–74} with the Davidson correction.⁷⁵ A large active space of $(8e,12o)$ —comprising eight A' and four A'' orbitals—was used together with the aug-cc-pVQZ basis set augmented by additional diffuse s and p functions.^{76,77} Transition dipole moments and the electronic orbital angular momentums were also calculated at the same level. The

resulting *ab initio* data were used to construct a four-state DPEM employing a NN-based adiabatic-energy diabatization scheme.⁶⁷ Symmetry constraints from the complete nuclear permutation-inversion (CNPI)⁷⁸ of H_2S were rigorously enforced to ensure correct coupling behavior near CIs. The neural network parameters were optimized via the Levenberg–Marquardt algorithm⁷⁹ by minimizing residuals between (i) adiabatic energies obtained from DPEM and *ab initio* values and (ii) DPEM elements and their target values obtained from *ab initio* data (explained in SI-I). The transition dipole moments were fitted by NN approach with 6 neurons in each of the two hidden layers (see SI-IV for more details). The final RMSEs for $1^1\text{A}'$ below 8 eV, $2^1\text{A}'$ below 9 eV, $3^1\text{A}'$ below 10 eV and $4^1\text{A}'$ below 11 eV are 26.7, 31.4, 33.2, and 60.1 meV, respectively. The distributions of *ab initio* energies and fitting errors of the four adiabatic states are shown in Figure S2(a) and (b). Using the DPEM, we performed quantum dynamics study of the nonadiabatic photodissociation process of the $3^1\text{A}'$ state using the Chebyshev real wave packet propagation method.^{80,81} In addition, TSH⁸² calculations on the same DPEM provide mechanistic insight into the dynamics. More details of the quantum dynamics and TSH calculations can be found in SI-V and SI-VI.

Table 1 lists the vertical excitation energies (VEE) of the three excited states, the VEE of $2^1\text{A}'$ and $3^1\text{A}'$ are 8.23 and

Table 1. Comparison of the Vertical Excitation Energies (in eV) of the $2^1\text{A}'$, $3^1\text{A}'$ and $4^1\text{A}'$ States of H_2S with Experimental and Previous Theoretical Results

	state			
	$1^1\text{A}'$	$2^1\text{A}'$	$3^1\text{A}'$	$4^1\text{A}'$
This work	0	8.23	8.82	9.03
(SC) ² -MR-SDCI ⁸⁷	0	8.24	8.77	8.81
RPA ⁸⁶	0	8.32	9.03	9.05
MDR-CI ⁶¹	0	7.97	8.69	8.70
CC-SE ⁸⁵	0	8.26	8.91	8.92
MRCI ²⁶	0	8.22	8.74	8.84
Experiment ^{14,83–85}	-	8.03, ⁸³ 8.19, ¹⁴ 8.27 ⁸⁵	8.80, ⁸³ 8.79 ⁸⁴	8.80, ⁸⁵ 8.81 ⁸³

8.82 eV, which are relatively close to previous theoretical calculations and experimental results.^{14,26,61,83–87} The asymptotic region of the two lowest $1^1\text{A}'$ states corresponding to the $\text{SH}(\text{A}^2\Sigma^+)$ or $\text{SH}(\text{X}^2\Pi)$ products are shown in Figure 1(a). To characterize the intersections among these states, the adiabatic potential energy curves for the four states at C_{2v} geometry as a function of $\theta_{\text{H-S-H}}$ were plotted in Figure 1(b). The minimum energy configurations of the CI seams and corresponding energies were listed in Table 2. Between the $2^1\text{A}'$ and $3^1\text{A}'$ states, there exists a CI at small bond angles ($\approx 51^\circ$) and an AVC at larger angles ($\approx 113^\circ$). The former has a higher energy than the latter. As depicted in Figure 1(c), the AVC (the marked elliptical regions) is connected to the linear potential well at 180° . At small angles, however, the presence of higher energy CI associated with the $3^1\text{A}'$ state (denoted as CI-3, labeled with purple line) creates a barrier. The combined influence of CI-3 and AVC gives rise to a shallow potential well in interaction region on the $2^1\text{A}'$ adiabatic PES, generating a unique U-shaped feature on the $2^1\text{A}'$ adiabatic PES that spans $r_{\text{SH}_1} = r_{\text{SH}_2} = 1.2$ – 1.6 Å and $\theta_{\text{H-S-H}} = 60$ – 120° . The center of this U-shaped basin lies near 8.23 eV (orange dot in Figure 1(c)). This topological feature is very different from H_2O ,

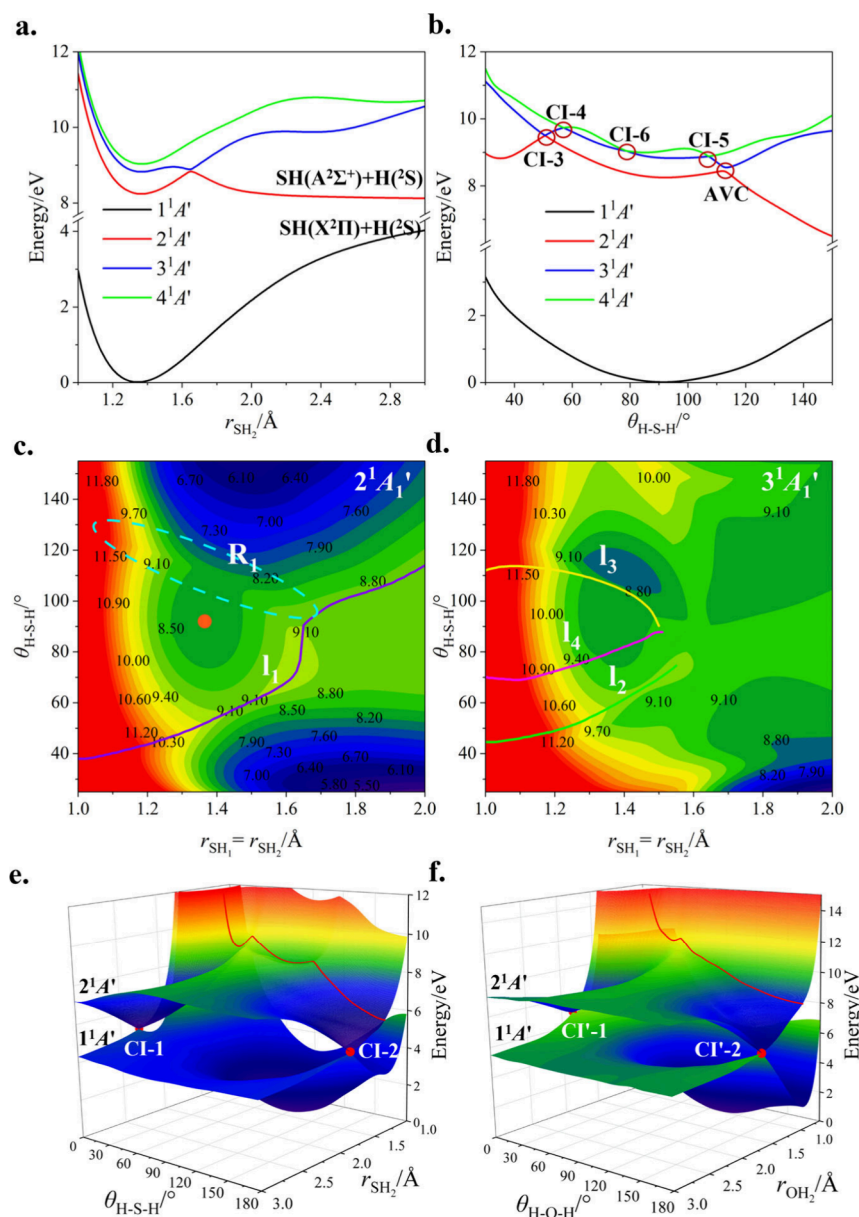


Figure 1. (a) Adiabatic potential energy curves as a function of one S–H bond length with $r_{SH_1} = 1.343$ Å and $\theta_{H-S-H} = 91.6^\circ$. (b) Curves along the C_{2v} line ($r_{SH_1} = r_{SH_2} = 1.343$ Å) at different bond angles θ_{H-S-H} . (c, d) Adiabatic PESs of the $2^1A'$ and $3^1A'$ states as functions of equivalent bond lengths and θ_{H-S-H} . Blue ellipses indicate AVC regions, colored lines mark CI seams and the orange dot denotes the center of the U-shaped structure. (e, f) Adiabatic PESs of the $2^1A'$ and $1^1A'$ states of H₂S and H₂O (unpublished results) with $r_{SH_1} = 1.343$ Å and $r_{OH_1} = 0.979$ Å, respectively. CI-1/CI'-1 and CI-2/CI'-2 correspond to the linear CIs at 0° and 180° , respectively. Red lines trace the C_{2v} potential energy curves for H₂S and H₂O.

Table 2. Calculated Geometries with the Lowest Energy along the CI Seam between Different States

CI	$\theta_{H-S-H}/\text{deg}$	$r_{SH_1}/\text{\AA}$	$r_{SH_2}/\text{\AA}$	E/eV	Theo. ²⁶ /eV
CI-1	0	1.66	2.57	4.60	4.45
CI-2	180	1.34	1.84	4.82	4.68
CI-3	60	1.49	1.49	9.08	
CI-4	66	1.46	1.46	9.44	
CI-5	106	1.37	1.37	8.85	
CI-6	81	1.39	1.39	8.98	

which as shown in Figure 1(f) and Figure S3. Although the $2^1A'$ and $3^1A'$ states of H₂O also display a CI at small angles and an AVC at larger angles, the angular separation between

them is much smaller, and the AVC region is broader along the angular coordinate (unpublished results). As a result, the $2^1A'$ PES of H₂O lacks the pronounced U-shaped basin characteristic of H₂S. Multiple CIs are also present between the $3^1A'$ and $4^1A'$ states and three such CIs as shown in Figure 1(b) and the CI seams are shown in Figure 1(d). Notably, both H₂S and H₂O exhibit a “double CI” between $2^1A'$ and $1^1A'$ states at 0° and 180° , as shown in Figure 1(e) and 1(f).

As mentioned above, theoretical studies on the absorption spectrum of H₂S have been focused on the lowest band, making the assignment of highly excited states uncertain. This work bridged this gap. Figure 2(a) compares our calculated total photoabsorption cross section of $3^1A'$ (1^1B_2 state)

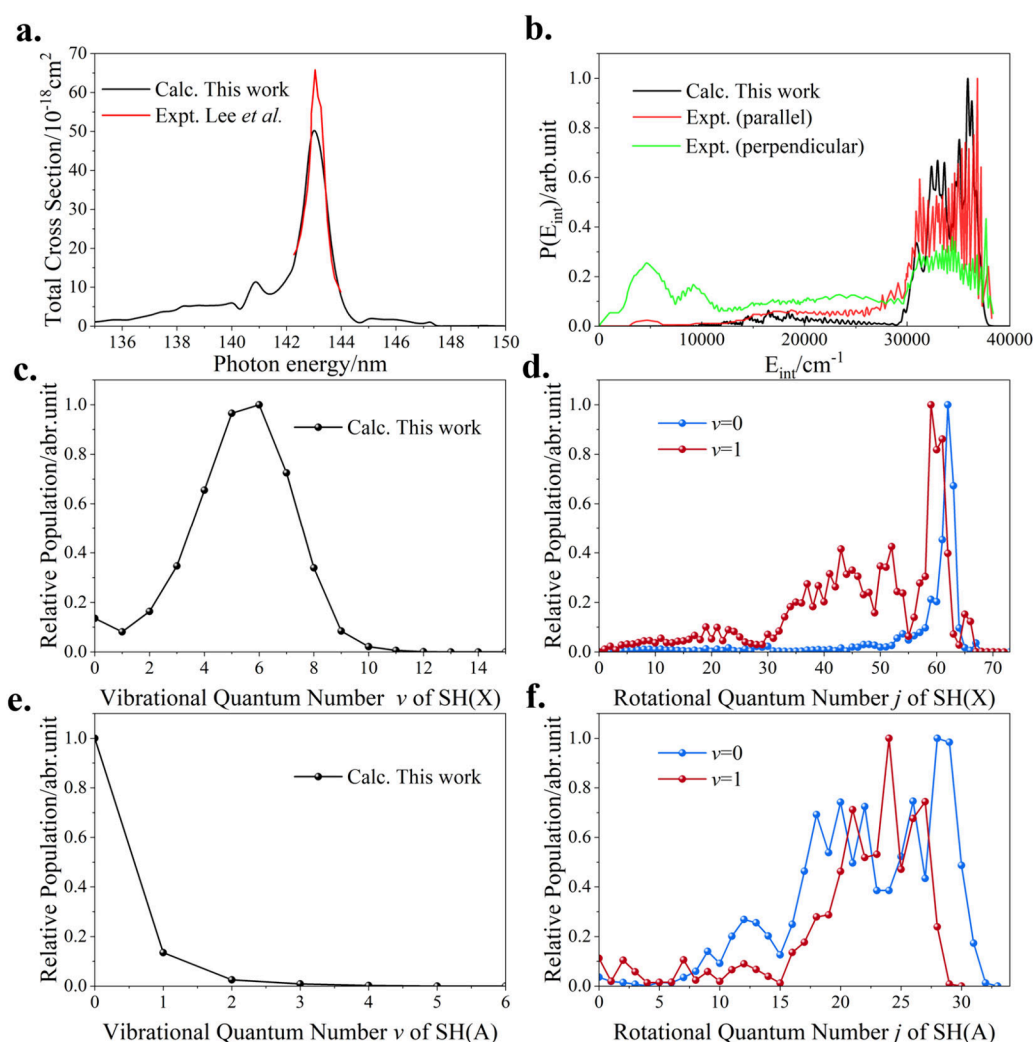


Figure 2. (a) The calculated total cross sections (black line, which was red-shifted by 1.5 nm (~ 0.09 eV)), compared with the measured absorption spectrum⁸⁸ (red line). (b) The distribution spectrum of internal energy of H+SH(X²Π/A²Σ⁺) product, in comparison with previous experimental results of Zhao et al.²⁶ The red and green solid lines denote the parallel and perpendicular signals, respectively. (c) The calculated vibrational state distribution and (d) rotational state distribution of product SH(X²Π, $\nu = 0, 1$) for the photodissociation. (e) The calculated vibrational state distribution and (f) rotational state distribution of product SH(A²Σ⁺, $\nu = 0, 1$) for the photodissociation.

compared with the measured absorption spectrum.⁸⁸ Note that the calculated absorption peak is slightly red shift by 1.5 nm (~ 0.09 eV) to match the experimental spectrum. The peak at ~ 143 nm was assigned to $(2b_1)^{-1}(nda_1)^1B_1 \leftarrow \tilde{X}^1A_1$, and the peak at ~ 140 nm was attributed to a combination of $(2b_1)^{-1}(nda_2)^1B_2 \leftarrow \tilde{X}^1A_1$ and $(2b_1)^{-1}(ndb_1)^1A_1 \leftarrow \tilde{X}^1A_1$ by Masuko and co-workers.⁸³ Based on our calculations, we propose a refined assignment. Specifically, the peak at ~ 143 nm originates from both the $(2b_1)^{-1}(nda_2)^1B_2 \leftarrow \tilde{X}^1A_1$ and $(2b_1)^{-1}(nda_1)^1B_1 \leftarrow \tilde{X}^1A_1$ transitions while the peak at ~ 140 nm is dominated by the $(2b_1)^{-1}(ndb_1)^1A_1 \leftarrow \tilde{X}^1A_1$ transition, as shown in Figure S9. Importantly, the calculated spectral width and absolute value shows good agreement with experiment, supporting the reliability of the constructed PESs and transition dipole moments.

The energy disposal of the photofragments provides further mechanistic insight into photodissociation. Figure 2(b) compares the calculated internal energy distribution spectrum ($P(E_{\text{int}})$) at the wavelength at 143.15 nm of the H+SH(X²Π/A²Σ⁺) products with previous experiment results of Zhao et al.²⁶ The experimental data show distinct signatures for

fragments detected parallel and perpendicular to the probe polarization. Our results are in good agreement with the parallel component, while the perpendicular signal—dominated by low internal energy—does not appear in our simulations. The perpendicular internal energy distribution of experimental data shows a pronounced distribution of low internal energy, which aligns more closely to the dynamical characteristic of the ¹A'' states (see Figure S12 and refs. 21 and 26). Therefore, we propose the following two possibilities: (i) via the Renner-Teller effect that coupled the ¹A'' states after exciting to the ¹A' states; (ii) co-excitation the ¹A'' states, given the energy proximity of the 6¹A'' states to the 3¹A' state (see SI–VIII. for more details of excitation energies and adiabatic absorption spectrum). We believe that the second mechanism is more likely, as the 6¹A'' state $\leftarrow$ 1¹A' transition is a perpendicular excitation which typically leads to products that are more likely to be perpendicular to the photon polarization, while the Renner-Teller pathway from Franck-Condon region to linear configuration would undergo strong anisotropic forces resulting the high internal energy product. The dominant contribution arises from high internal energy

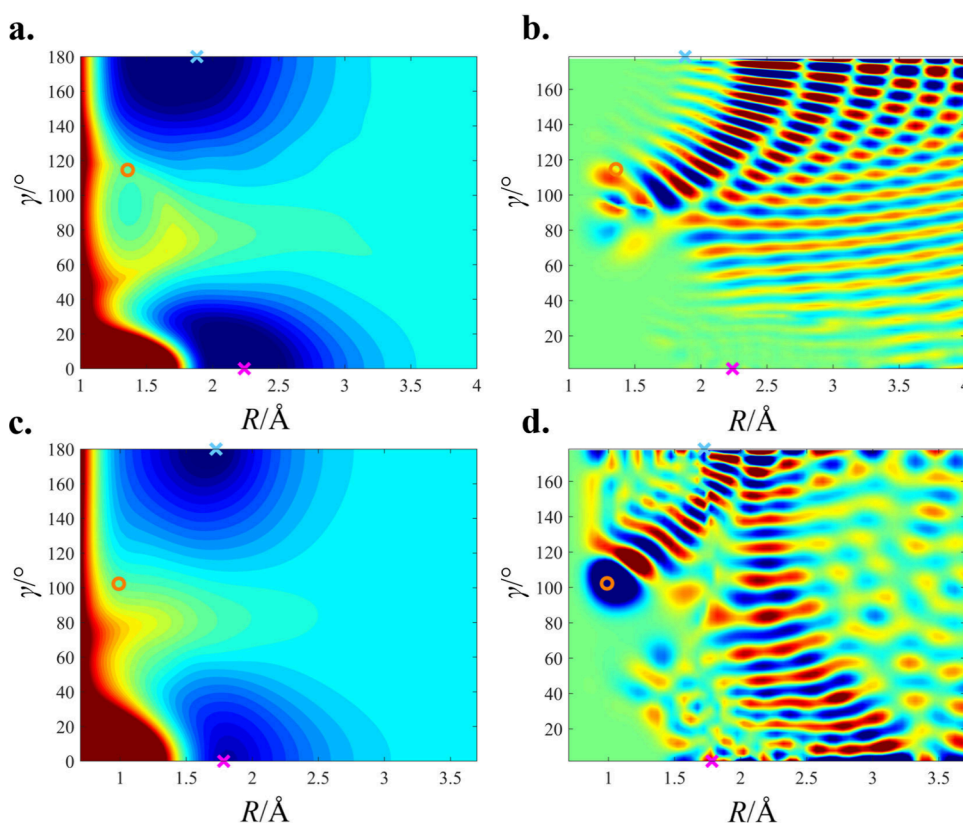


Figure 3. (a, c) The adiabatic PESs of $2^1A'$ of H_2S and H_2O ⁸⁹ in Jacobi coordinate, with r fixed in 1.343 $\text{\AA}$ for H_2S and 0.979 $\text{\AA}$ for H_2O , respectively. (b) and (d) The wave functions on $2^1A'$ state of H_2S and H_2O , respectively. The orange circles indicate the starting points of the wave function of $SH(A^2\Sigma^+, \nu = 0)$ and $OH(A^2\Sigma^+, \nu = 0)$ in $2^1A'$ state.

product corresponding to $SH(A^2\Sigma^+)$, while the fraction associated with $SH(X^2\Pi)$ at lower internal energies is relatively minor (the branching ratio obtained from quantum dynamics is shown in Figure S(11)). This result is consistent with the dynamics at wavelength of 121.6 nm,^{15,22} where dissociation also proceeds via the $2^1A'$ state. Figures 2(c) and 2(d) display the calculated vibrational and rotational state distribution of $SH(X^2\Pi)$. The vibrational state distributions of the $SH(X^2\Pi)$ product are highly excited, with the maximum vibrational population occurring at $\nu = 6$. This contrasts sharply with $OH(X^2\Pi)$ formed in water photodissociation, where the ground vibrational state dominates.^{35,55–57,89,90} The rotational distributions of $SH(X^2\Pi)$ also exhibit strong excitation due to the torque exerted by the dissociation PES, peaking at $j = 62$ for $\nu = 0$ and at $j = 59$ for $\nu = 1$, respectively. In comparison, the vibrational state distribution of $SH(A^2\Sigma^+)$, shown in Figure 2(e), is much colder, with a sharp maximum at $\nu = 0$ followed by a monotonic decrease at higher ν . The $SH(A^2\Sigma^+)$ fragments are less rotationally excited: for both $\nu = 0$ and 1, the distributions peak at $j = 28$ and $j = 24$, respectively (Figure 2(f)). Since the $SH(X^2\Pi)$ fragment formation from transitions at the collinear HSH and HHS CIs between the $1^1A'$ and $2^1A'$ states, it is not surprising that the strong torsional force along the angle resulting in rotational excitation in the $SH(X^2\Pi)$ product, a similar mechanism is responsible for the high rotational excitation $OH(X^2\Pi)$ in water dissociation.^{35,89,91,92} Nevertheless, the key questions remain: what drives the dominance of $SH(A^2\Sigma^+)$ as the primary product?

To unravel the mechanism underlying the dominance of $SH(A^2\Sigma^+)$ and these product energy distributions, we first examine the wave functions on the $2^1A'$ state PES. To isolate a

specific product channel, the total wave function was projected onto the $SH(A^2\Sigma^+, \nu = 0)$ manifold by integrating over the internuclear distance. As shown in Figures 3(a) and 3(b), the projected wave function displays pronounced amplitude along the U-shaped structure of the PES, extending from the basin region toward linear geometries. This pattern indicates that molecules undergo nonadiabatic transitions via the $3^1A' \rightarrow 2^1A'$ AVC, then proceed through the basin, and ultimately exit within a confined range of bond angles. At linear geometries, the amplitude does not coincide with the $2^1A' \rightarrow 1^1A'$ CI but instead shows a slight deviation, which can be traced back to the exit angle of the U-shaped pathway. This indicates that access to the $2^1A' \rightarrow 1^1A'$ CI is not angularly favorable, thereby explaining the low yield of $SH(X^2\Pi)$. By contrast, in H_2O photodissociation the wave function on the $2^1A'$ state is localized at the CI, thus favoring $OH(X^2\Pi)$ formation due to the absence of a basin structure, as shown in Figures 3(c) and 3(d).

This wave function picture is reinforced by TSH analysis at the same total energy (9.174 eV, sum of zero point energy and excitation energy), and the calculated $SH(A^2\Sigma^+)/SH(X^2\Pi)$ branching ratio obtained through TSH calculation is 3.18, demonstrating a predominant production of the $SH(A^2\Sigma^+)$ product, which is consistent with the branching ratio of 4.69 obtained from quantum dynamics calculation. As shown in Figures 4(a) and 4(b), most trajectories leading to the $SH(A^2\Sigma^+)$ product become temporarily trapped in the basin before escaping through the open channel of the U-shaped structure. In contrast, trajectories leading to the $SH(X^2\Pi)$ product exhibit more complex dynamics as shown in Figures 4(a) and 4(b): after escaping the basin, they evolve toward the

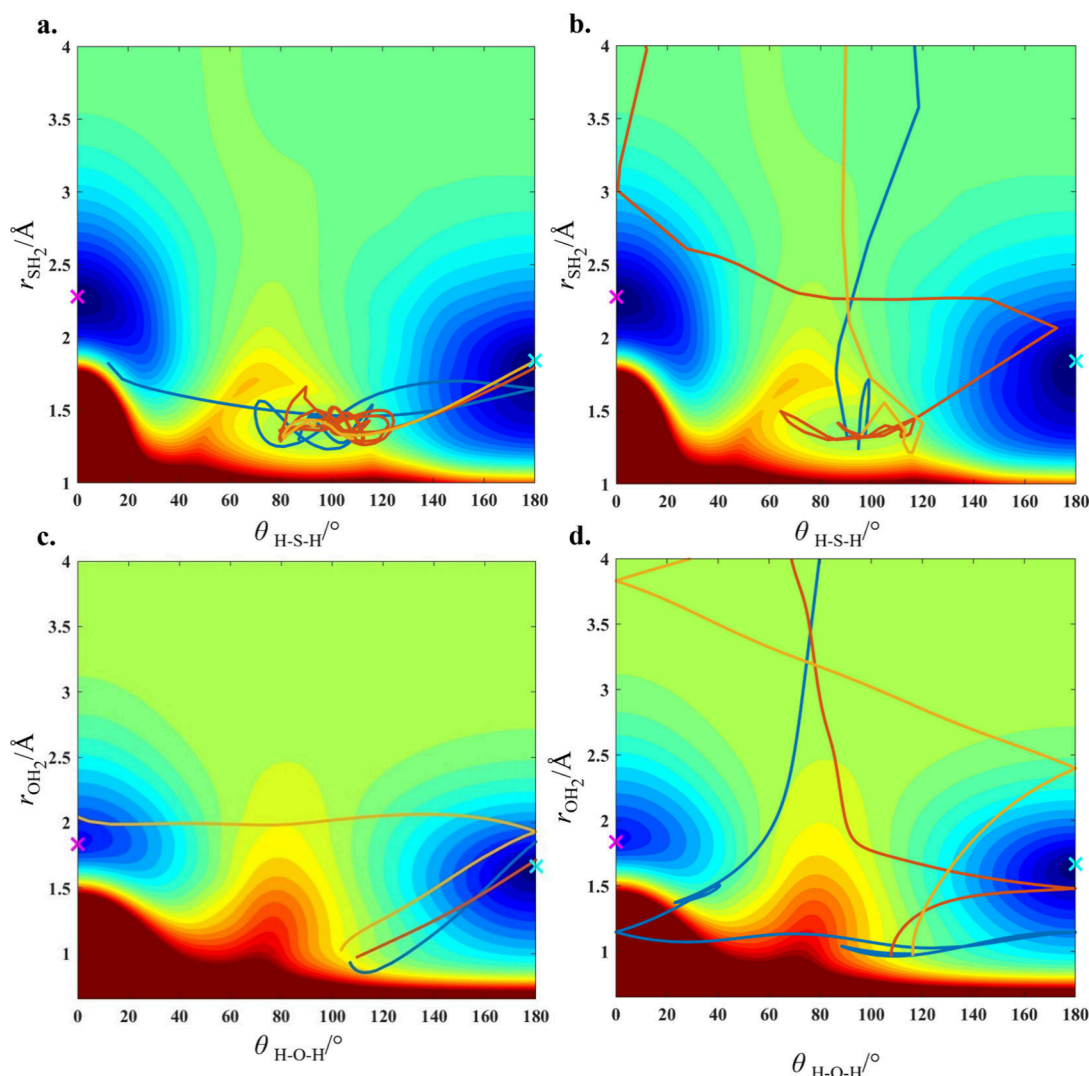


Figure 4. (a) Three typical trajectories forming SH($X^2\Pi$) product plotted on the adiabatic PESs of $2^1A'$ states of H_2S . (b) Same as (a) but for SH($A^2\Sigma^+$)-forming trajectories. (c) Three typical trajectories forming OH($X^2\Pi$) product plotted on the adiabatic PESs of $2^1A'$ state of H_2O .⁸⁹ (d) Same as (c) but for OH($A^2\Sigma^+$)-forming trajectories.

linear potential well near either the HSH or HHS collinear configuration, undergo a nonadiabatic transition to the $1^1A'$ PES, and subsequently dissociate to yield SH($X^2\Pi$) product. Thus, the SH($A^2\Sigma^+$)/SH($X^2\Pi$) branching ratio is largely determined by the bond angle of escape from the basin, which is influenced by transient energy disposal across different modes. Only trajectories with sufficient bending vibrational energy can access the $2^1A'-1^1A'$ CI. For H_2O , the situation is different: due to the repulsive characteristic of the $\tilde{B}$ state PES in the interaction region, the trajectories undergo a fast evolution to the potential well formed by HOH CI. The OH($A^2\Sigma^+$)-producing trajectories dissociate across a wide range of bond angles, while the dissociation leading to SH($A^2\Sigma^+$) is more narrowly directed.

The transient energy-dependent angles of escape from the basin can be quantified by the correlation between R_{linear} and $T_{\text{rot-j}}$ obtained from TSH, where R_{linear} denote the distance between the dissociative H atom and the center mass of nondissociative SH diatom when the configuration first approaches to HSH linearity in the $2^1A'$ state. Thus, it reflects whether a trajectory reaches the vicinity of the HSH2 $^1A'-1^1A'$ CI (the HHS geometry CI is not important as can be seen

from negligible amplitude in Figure 3(b)). Trajectories that never reach linearity are also included, with their maximum bond angle are treated as first approach to linearity. These typically occur at large R_{linear} , indicating bypass the $2^1A'-1^1A'$ CI entirely. $T_{\text{rot-j}}$ represents the transient rotational kinetic energy of the SH diatom at R_{linear} (the definition of $T_{\text{rot-j}}$ is provided in the SI-VII). This energy is determined by the bending vibrational mode and directly related to the rotational energy of the product fragment in the asymptotic region. As shown in Figures 5(a) and 5(b), SH($X^2\Pi$)-forming trajectories cluster near shorter R_{linear} in the vicinity of CI and higher $T_{\text{rot-j}}$ (high bending vibration), which quantitatively supports the mechanism that only sufficient bending vibrational energy can access to the nearby CI. In contrast, SH($A^2\Sigma^+$) forming trajectories are predominantly concentrated in the asymptotic region at larger R_{linear} , which is far away from the CI, associated with a lower $T_{\text{rot-j}}$. After escaping from the basin, lower rotational kinetic energy trajectories bypass the CI and proceed directly to dissociation along the $2^1A'$ PES, yielding SH($A^2\Sigma^+$). Consequently, the high rotational energy excitation of SH($X^2\Pi$) via the $2^1A'-1^1A'$ CI and the SH($A^2\Sigma^+$)/SH($X^2\Pi$) branching ratio is governed by these distinctive topological

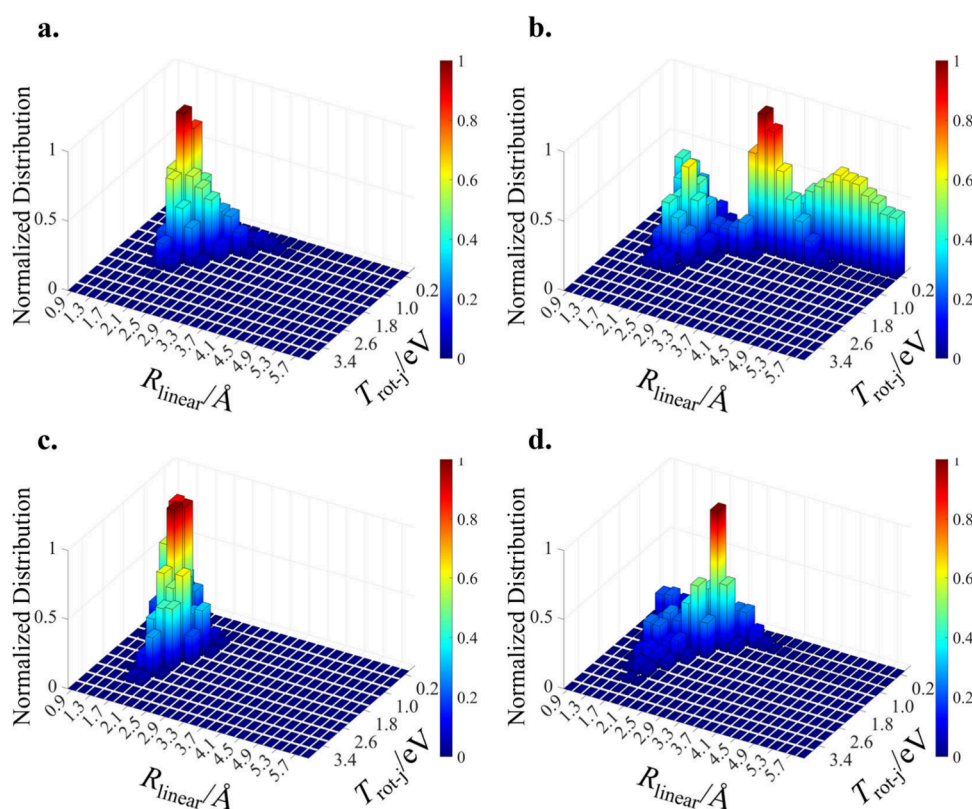


Figure 5. (a, b) The correlation between the product distribution of R_{linear} and $T_{\text{rot-j}}$ for the $\text{SH}(X^2\Pi)$ -producing and $\text{SH}(A^2\Sigma^+)$ -producing trajectories when they are closest to the linear H–S–H configuration. (c, d) Correlation between the product distribution of R_{linear} and $T_{\text{rot-j}}$ for the $\text{OH}(X^2\Pi)$ -producing and $\text{OH}(A^2\Sigma^+)$ -producing.

features of the PES. The conclusions drawn by Cook et al.²² from classical trajectory simulations on two-dimensional adiabatic PESs are consistent with our findings. Figure 5(c) and 5(d) show that H_2O exhibits only slight difference between $\text{OH}(X^2\Pi)$ - and $\text{OH}(A^2\Sigma^+)$ -forming trajectories. In H_2O , by contrast, the absence of a basin-like structure means dissociation proceeds directly to the linear CI, making nonadiabatic transitions the primary determinant of the branching ratio. Our calculated results indicate that the $\text{SH}(A^2\Sigma^+, \nu = 0)$ fragment constitutes 70% of the total product yield, confirming that most products originate from a single, basin-mediated pathway.

To summarize, we present a DPEM for the lowest four $1A'$ states of H_2S , utilizing high-level *ab initio* data and the adiabatic-energy based diabaticization method within neural networks. The total cross section and internal energy distribution obtained from quantum photodissociation dynamics calculations align well with experiment, validating the accuracy and reliability of our PESs. Despite the similarity in the CIs between the $1^1A'$ and $2^1A'$ states of H_2S and H_2O , our quantum dynamics calculation of H_2S at 143.15 nm yields products rovibrational populations and branching ratios that diverge markedly from those of H_2O . TSH calculations reveal that the disparity in the PESs of the $2^1A'$ state within the interaction region is the primary determinant of these dynamical differences. Two nearby intersections generate a basin on the $2^1A'$ PES of H_2S that directs most trajectories with lower rotational kinetic energy to dissociate on the excited surface through a narrow range of bond angles along the escape pathway, yielding $\text{SH}(A^2\Sigma^+)$. In contrast, a minor fraction of H atoms with higher rotational energy rapidly

reached the linear CI and undergo nonadiabatic transition to the ground state, yielding $\text{SH}(X^2\Pi)$ products.

While previous studies have recognized that CI-induced topological features—such as a local barrier^{93–96} or well⁹⁷—can influence reaction dynamics, they typically focused on the effect of a single CI. Our results reveal a new mechanistic regime in which multiple nonadiabatic intersections cooperatively shape the PES topology, creating a dual-barrier basin that governs both trapping and product branching. This finding establishes a new conceptual framework for understanding photodissociation dynamics in high-lying electronic states, where multi-intersection topology, rather than a single CI, dictates the outcome of nonadiabatic molecular processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.5c03400>.

Details of the construction of diabatic potential energy matrix and transition dipole surface, theory of quantum dynamics calculation and trajectory surface-hopping calculation, definition of the rotational kinetic energy of SH diatom $T_{\text{rot-j}}$, and discussion on the absorption peak positions (PDF)

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Notes

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