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Exploring the Dynamics of the Photoinduced Ring-Opening of Heterocyclic Molecules

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Supporting Information

ABSTRACT: Excited states formed by electron promotion to an antibonding σ* orbital are now recognized as key to understanding the photofragmentation dynamics of a broad range of heteroatom containing small molecules: alcohols, thiols, amines, and many of their aromatic analogues. Such excited states may be populated by direct photoexcitation, or indirectly by nonadiabatic transfer of population from some other optically excited state (e.g., a ππ* state). This Perspective explores the extent to which the fast-growing literature pertaining to such (n/π)σ*-state mediated bond fissions can inform and enhance our mechanistic understanding of photoinduced ring-opening in heterocyclic molecules.

All but a few very small molecules absorb near-ultraviolet (UV) photons. Absorption results in formation of electronically excited molecules, which can display a diverse range of photophysical behaviors. Some molecules are remarkably photostable, and return to their ground state by fluorescence. Dye molecules (fluorophores) such as those used in dye lasers, in single molecule spectroscopy, and in super-resolution imaging constitute obvious examples.1–5 Other molecules like the DNA bases6 or commercial sunscreen ingredients like avobenzene, oxybenzone, or many cinnamate derivatives7 have extremely short-lived excited states, show no fluorescence, and yet are also deemed photostable. In these cases, the excited state molecules find efficient nonradiative decay paths back to the ground state. Such nonradiative decay depends on nuclear distortions that bring the potential energy surfaces (PESs) for the excited and ground electronic states of the molecule into near degeneracy, i.e., so-called regions of conical intersection (CI) between the PESs.8–12 Examples of nuclear motions that enable excited state population to funnel through such CIs include intramolecular proton transfers (e.g., keto ↔ enol-isomerism), cis- ↔ trans-isomerism, and, in the case of cyclic molecules, out-of-plane ring distortions. Photostability in these cases requires that (i) the excited state PES has an appropriate topology, specifically that there is no significant energy barrier between the geometry at which the photoexcited molecule is prepared and that of the CI, and (ii) the nuclear distortions driving the internal conversion (IC) process are eventually “corrected” after crossing to the ground state PES, thereby ensuring that the molecule suffers no net change as a result of the excitation—recovery cycle.7

Photodamage—wherein the starting molecule is effectively transformed or destroyed—is another limiting fate of UV photon absorption. Photoinduced bond fission (i.e., photodissociation) is a common example of such a process, and is the theme of this Perspective. Many recent studies have recognized the key roles of (n/π)σ* states in enabling excited state bond fissions.13 These are states formed by promoting an electron from a lone pair (n) or bonding (π) molecular orbital to an antibonding σ* orbital, which, from here on, will often simply be generically labeled as πσ*. One further aspect of book keeping: throughout, labels like πσ* will be reserved for diabetic states, and S0, S1, S2, etc. are used when referring to the adiabatic singlet states.

The lead players (molecules) in this Perspective—dimethyl-sulfide (MeSMe), thioanisole (PhSMe), thiophene, and various thiophene derivatives—are shown in Figure 1. The Perspective starts by summarizing aspects of the near UV photochemistry of MeSMe and PhSMe in the gas phase. Both molecules contain a C–S–C linkage and undergo πσ*-state-mediated S–C bond fission. Thioanisole (and thiophenols) have been featured in recent studies aimed at determining the extent to which dynamical insights from gas phase studies can inform our knowledge and understanding of the early time dynamics induced by UV photoexcitation of the corresponding molecules in solution. The parallels revealed by such comparative studies, in turn, encourage the use of solution-phase samples and ultrafast pump–probe transient absorption (TA) methods to demonstrate πσ*-state-mediated S–C bond extension and fission in heterocycles like 2(5H)-thiophenone (2-thiophenone from hereon)—a simple five-membered heterocyclic α-carbonyl compound that...
also contains a C–S–C linkage. We conclude by returning to the gas phase and surveying recent progress in exploring dynamical aspects of the photoinduced ring-opening of other thiophene derivatives and, then, of other cyclic molecules.

Gas Phase Photochemistry of MeSMe and PhSMe. Figure 2 shows cuts through the PESs for the ground and first few excited singlet states of MeSMe, PhSMe, and thiophene, along one S–C bond. The PECs for extending an S–Me bond ($R_{S-Me}$) in dimethylsulfide shown by red lines in Figure 2a apply for the ground state equilibrium geometry ($\angle CSC \sim 99^\circ$). The ground state of MeSMe has $1A'$ symmetry (in $C_2v$) and, at this bent geometry, its PEC correlates with ground (X)-state Me and MeS radical products. The first excited state, a dissociative state of $1A''$ symmetry formed by excitation from the highest occupied molecular orbital (HOMO), the $S(3p_x(a'''))$ orbital, to a $\sigma^\#(a')$ orbital localized along one S–Me bond, correlates to this same limit. This is one of two near-degenerate states of $1A''$ symmetry reached by vertical excitation from the ground state minimum energy geometry (the other state has substantial Rydberg character). The diabatic PECs for these two $1A''$ states exhibit a conical intersection at small $R_{S-Me}$ (labeled CI-1 in Figure 2a), and the interaction of these two $1A''$ states is revealed by the diffuse resonance structure apparent in the parent absorption spectrum.14,15 Figure 2a shows one higher energy PEC as a red line. This is for a dissociative $1\pi\sigma^\#$ state of $1A'$ symmetry that, at bent geometries, correlates to ground-state Me(\(\bar{X}\)) plus electronically excited (\(\bar{A}\) state) MeS products. The starting orbital in this case is an in-plane $\sim sp^2(a')$ orbital on the S atom.

Note, these PECs are just what is implied by the acronym: one-dimensional cuts through multidimensional PESs, which may—and in this case do—have very different topographies in other coordinate systems. This is illustrated by the black lines in Figure 2a, which show the corresponding potentials when $\angle CSC = 180^\circ$. In this higher symmetry (linear) limit, the ground state of MeSMe has the term symbol $1\Sigma^+$, and its PEC correlates diabatically with Me(\(\bar{X}\)) + MeS(\(\bar{A}\)) products. The S atom in the MeS radical supports five nonbonding electrons, distributed between two p ($\pi$) orbitals and an on-axis sp-hybrid ($\sigma$) orbital. Viewed in this way, the $\bar{X}$ and $\bar{A}$ states of the MeS radical have respective configurations $\pi\sigma^2$ and $\pi\sigma^2\pi^*$ and, as Figure 2a shows, the collinear approach of ground state Me and MeS radicals results in a repulsive interaction. This is the long-range part of a $1\Pi$ excited state of (linear) MeSMe formed by $\sigma^\# \leftarrow \pi$(HOMO) promotion, which splits into the dissociative $1A'$ and $1A'$ states on bending the C–S–C frame. As Figure 2a also shows, the former potential is (relatively) unaffected by such bending, whereas the latter forms a conical intersection (CI-2 in Figure 2a) with the ground state PES. Interested readers are referred to ref 13 for more examples of the importance of such $\sigma\pi^\#$ states in the excited state photochemistry of numerous molecular prototypes.

S–Me bond fission following near-UV photoexcitation of jet-cooled MeSMe has been investigated by velocity map imaging (VMI) methods.15,16 Figure 3a,b shows images of the Me and MeS fragments formed by photoexcitation of jet-cooled MeSMe molecules at 227.5 nm and detected using “universal” (118 nm) photoionization. Both images are annular, confirming that the fragments are formed translationally excited. The radial distribution in each image allows determination of the respective fragment recoil velocities, confirms that the two sets of products are momentum matched, and allows calculation of the total kinetic energy of the Me + MeS products. Energy conservation considerations confirm that both fragments are formed in their electronic ground states. The

**Figure 1.** Equilibrium structures of dimethylsulfide, thioanisole, thiophene, 2-thiophenone, and 2-bromothiophene, highlighting the C–S–C motif common to all five species, with S, C, O and Br atoms represented in yellow, black, red, and purple, respectively.

**Figure 2.** Calculated PECs along the S–C bond highlighted in the accompanying structure for the ground and first few singlet excited states of (a) MeSMe, at its equilibrium bent geometry (red lines) and at $\angle CSC = 180^\circ$ (black lines), (b) PhSMe, and (c) thiophene—both at planar geometries. Solid and dashed lines are used to distinguish states of $A'$ and $A''$ symmetry, respectively, and conical intersections CI-1 and CI-2 are indicated in each case. Further details are provided in the Supporting Information.
These moment for which lies perpendicular to the molecular plane. Distribution consistent with prompt Me fragments are formed in their zero-point (σ*) orbitals of the S atom in the PhS radical are not degenerate, as the 3pσ orbital conjugates with the π-system of the ring. The parent → product correlations in this case can be derived by focusing on just three electrons in these S 3pσ(a∗) and 3pσ(a∗) orbitals of the radical. The Σ and Α states of PhS can be represented by the respective configurations (a∗)(a∗) and (a∗)(a∗)2. The in-plane approach of ground-state PhS and Me radicals results in a repulsive interaction which, again, can be attributed to the long-range part of the diabatic 1ππ* PEC. The ground and 1ππ* PECs again exhibit a conical intersection (CI-2 in Figure 2b) at extended Rc–Me. Figure 2b also shows that the lowest singlet state of PhSMe reached by photoexcitation is actually the first 1ππ* state, the PEC for which shows a conical intersection (CI-1) with the 1ππ* state at small Rc–Me. Both CIs become regions of avoided crossing as the molecule distorts from planar.

Several VMI studies of the Me(ν = 0) fragments resulting from near UV photoexcitation of thioanisole and substituted thioanisoles have been reported, and full-dimensional PESs and state-couplings for the three states of PhSMe featured in Figure 2b are also available. Focusing specifically on bare PhSMe, molecules in the 1ππ*(ν = 0) level decay so slowly (nsec time scale) that the parent absorption spectrum shows resolved rovibrational structure. Nonetheless, molecules in this level do predissociate. Me radicals are formed and, as Figure 3c shows, these can be imaged. The Me(ν = 0) fragments are formed translationally excited with, in this case, a near-isotropic recoil velocity distribution (consistent with the long excited state lifetime). Again, the relative narrowness of the annular ring indicates that the partner PhS fragments are formed in a fairly narrow spread of internal energy states; more detailed analysis reveals that >90% of them are formed in the excited (Α) electronic state.

These observations are all consistent with the dissociation dynamics implied by the PECs shown in Figure 2b. Population excited to the 1ππ* state first has to transfer to the 1ππ* continuum by nonradiative coupling in the region of CI-1. Viewed from the perspective of PhSMe molecules in the 1ππ*(ν = 0) level, CI-1 presents an energy barrier.

Now consider S–Me bond fission following near UV excitation of thioanisole, the equilibrium geometry of which has all the heavy atoms in a plane, with ∠CSC ~ 104°. In this high symmetry limit, the ground state PEC correlates diabatically with a Me radical and electronically excited PhS(Α) products (Figure 2b). In contrast to MeS, the 3pσ and 3pσ orbitals of the S atom in the PhS radical are not degenerate, as the 3pσ orbital conjugates with the π-system of the ring. The parent → product correlations in this case can be derived by focusing on just three electrons in these S 3pσ(a∗) and 3pσ(a∗) orbitals of the radical. The X and Α states of PhS can be represented by the respective configurations (a∗)(a∗)1 and (a∗)(a∗)2. The in-plane approach of ground-state PhS and Me radicals results in a repulsive interaction which, again, can be attributed to the long-range part of the diabatic 1ππ* PEC. The ground and 1ππ* PECs again exhibit a conical intersection (CI-2 in Figure 2b) at extended Rc–Me. Figure 2b also shows that the lowest singlet state of PhSMe reached by photoexcitation is actually the first 1ππ* state, the PEC for which shows a conical intersection (CI-1) with the 1ππ* state at small Rc–Me. Both CIs become regions of avoided crossing as the molecule distorts from planar.

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The simple few-electron picture used to rationalize CI-2 and the electronic branching in the radicals formed upon S–Me bond fission in PhSMe can be extended to show how analogous photoinduced S–C bond extension in S-containing heterocycles can promote nonadiabatic population transfer (i.e., internal conversion) to the S0 PES and, potentially, result in ring-opening. To this end, Figure 4a shows the occupancy of key orbitals in the ground and 1πσ* excited states of PhSMe, and in the Me + PhS(X/Å) products. The key occupied orbitals in PhSMe(S0) are taken as the nonbonding 3p(α') orbital and the σS-Me(α') orbital localized on the bond that is destined to break. In this representation, the ground state parent molecule has configuration (α')2(α'')2, the dissociative 1πσ* state is described as (α')2(α'')2(σS-Me*, α')1, the X and Å states of the PhS radical have respective configurations (α')2(α'')1 and (α')2(α'')2, and the parent → product correlations for planar geometries are as shown in Figure 2b.

Figure 4c shows analogous PECs for (planar) thiophene, with the key σ and σ*(α') orbitals centered on one S–C bond. As Figure 4b shows, photoinduced rupture of this bond following population of the 1πσ* state would, in a diabatic picture, result in a biradical with α' symmetry, and we can anticipate a conical intersection between this and the S0 PES upon extending one S–C bond. Again, this is labeled CI-2, since the long wavelength UV absorption of thiophene involves π* ← π excitation and the resulting 1πσ* state population can access the 1πσ* state via a CI between the 1πσ* and 1πσ* PESs (CI-1) at shorter R_s-C bond lengths, as shown in Figure 2c. Support for this predicted ring-opening following UV photoexcitation of thiophene and nonadiabatic coupling to the ground state PES at CI-2 is provided by more rigorous electronic structure calculations23–25 and (indirectly) by the results of photofragment translational spectroscopy (PTS) experiments employing universal (synchrotron) vacuum UV (VUV) photoionization detection following 193 nm photoexcitation,26 and by both time-resolved photoelectron27 and resonance Raman28 spectroscopy studies.

Recent ultrafast UV pump, broadband TA probe studies in solution offer some of the most direct evidence for the formation of ring-opened products following UV excitation of such heterocycles.

Photochemistry of PhSH and PhSMe in Solution. Recent ultrafast UV pump, broadband TA probe studies in solution offer some of the most direct evidence for the formation of ring-opened products following UV excitation of such heterocycles. Before presenting data from such studies, however, it is necessary to consider the extent to which photophysical insights derived from gas phase studies can usefully inform our understanding of the corresponding system in solution, and vice versa, since the transferability between these very different environments is not immediately obvious. The photodissociation of an isolated gas-phase molecule can be viewed as a closed problem: energy and momentum are conserved, and any bond fission is irreversible. The same is not true in the solution-phase. The proximal solvent molecules may modify the PESs relative to those of the isolated solute molecule. Interaction with solvent molecules may dissipate some of the photoexcitation energy prior to bond fission, and will dissipate any excess energy partitioned into the dissociation products. Products that have no analogue in the corresponding gas-phase study may also arise by, for example, geminate recombination.

Nonetheless, there is growing literature showing that gas phase studies can provide a useful guide to the early time photofragmentation dynamics of the corresponding solute.
molecule in a weakly interacting solvent. Thiophenols have proven popular test-systems. For example, the H atoms formed in the near UV photolysis of gas-phase 4-methylthiophenol (4-MePhSH) molecules display an anisotropic, bimodal velocity distribution. Theory returns PECs along $R_{\text{S-H}}$ similar to those shown for PhSMe in Figure 2b, though the energy barrier under CI-1 (from the $^3\pi\pi^*$ ($v = 0$) level) is smaller. Analyses of data recorded at different excitation wavelengths indicate photoexcitation to the $^3\pi\pi^*$ and $^3\pi\sigma^*$ states, prompt S–H bond fission on the $^3\pi\pi^*$ PES (on a time scale that is short compared to the period of molecular rotation) and formation of both $\tilde{X}$ and $\tilde{A}$ state 4-MePhS radical products. Ultrafast pump–probe TA measurements following 267 nm excitation of 4-MePhSH in cyclohexane solution show an absorption centered at $\sim 480$ nm appearing within the $\sim 100$ fs instrument response time. This transient absorption is attributable to 4-MePhS($\tilde{X}$) radicals, and signifies prompt photoinduced S–H bond rupture (as in the gas phase); it narrows and declines in amplitude with increasing pump–probe time delays, $t$. The narrowing reflects the dissipation of vibrational energy from the nascent radical products to the solvent bath, while the decreasing amplitude is a signature of geminate recombination. Careful scrutiny of the TA spectra reveals a feature at very early $t$ attributable to 4-MePhS($\tilde{A}$) products—an outcome that, again, broadly mimics the gas phase photophysics. These electronically excited radicals are all quenched to their ground state by $\sim 300$ fs. Another absorption feature, at $\sim 380$ nm, grows over a longer time scale, and shows the same kinetics as the (partial) decay of the 4-MePhS($\tilde{X}$) radical signal. This $\sim 380$ nm band is attributable to a tautomer (cyclohexa-2,4-(or 2,5-) diene-1-thione) of 4-MePhSH formed by geminate recombination of the primary photoproducts.

Time-resolved infrared (TRIR) absorption studies following 267 nm excitation of 4-MePhSH also reveal prompt formation of 4-MePhS($\tilde{X}$) radical products, with an out-of-equilibrium vibrational state population distribution. Again, the evolving spectral profile reflects the relaxation of this product vibrational excitation through interaction with the solvent. The TRIR measurements also provide a direct probe of the parent ground state population. UV photoexcitation introduces “bleach” features in the IR TA spectrum, that partially recover with increasing $t$. This recovery confirms that geminate recombination leads not just to the above tautomer but also to some regeneration of the 4-MePhSH precursor. Nonetheless, the finding that the parent bleach does not fully recover indicates some “photodamage”, and the late-time observation of 4-MePhS($\tilde{X}$) radical absorption confirms that some primary photoproducts escape the primary solvent cage and remain separated from the geminate partner.

TRIR spectra following UV photolysis of 4-MePhSMe (in acetonitrile-$d_3$) show similarities, but also one notable difference. As with 4-MePhSH, bleach features due to photoinduced depopulation of the parent $S_0$ state are evident at the earliest $t$, and a (weak) absorption attributable to 4-MePhS($\tilde{X}$) radicals (formed by $S$=Me bond fission in this case) grows with increasing $t$. However, these TRIR spectra also show another, intense, absorption attributable to 4-MePhSMe molecules in their $^3\pi\pi^*$ state. This excited state absorption shifts to higher frequencies at early $t$ (reflecting the vibrational relaxation of the 4-MePhSMe($^3\pi\pi^*$) molecules) and decays to zero by $t \sim 1.5$ ns. Kinetic analysis returns solvent-dependent rate coefficients, but the principal findings are that the dissociation rate constant for 4-MePhSMe($^3\pi\pi^*$) molecules scales with the internal (vibrational) excitation and is always much smaller than that for 4-MePhSH($^3\pi\pi^*$) molecules. Both findings mirror trends in excited state lifetime found in gas-phase studies of thiophenols and thioanisoles, and can be understood in light of the potential barrier associated with CI-1 (Figure 2b).

**Dynamics of Photoinduced Ring-Opening in Solution.** As already noted, orbital correlation arguments (Figure 4b) and ab initio theory (Figure 2c, and refs 23–25) suggest that $^3\pi\pi^*$-state-mediated asymmetric ring-expansion constitutes a route by which photoexcited thiophene molecules can couple to the $S_\text{0}$ PES and ring-open. Stenrup and others have also identified a rival IC pathway initiated by out-of-plane deformation at the S atom, and qualitatively similar ring-puckered $^1\pi\pi^*/S_\text{0}$ Cls have also been reported for various substituted thiophenes. Experimental studies capable of revealing the dynamics of photoinduced ring-opening processes are still in their infancy, however. The challenges are substantial. Near-UV photoexcitation of thiophene typically populates a $^3\pi\pi^*$ state. Such population can access the $^3\pi\pi^*$ PES by nonadiabatic coupling in the region of CI-1, evolve toward CI-2 by extending $R_{\text{S-C}}$ further, transfer to the $S_\text{0}$ PES and complete the ring-opening. The available experimental data suggests that the initial coupling out of the $^3\pi\pi^*$ state (e.g., via CI-1) is an ultrafast process ($<100$ fs). Given the topography of the $^3\pi\pi^*$ PES, the subsequent evolution toward CI-2 is also likely to occur on a time scale characteristic of a molecular vibration. The initial ring-opened species is an isomer of the starting heterocycle, so cannot be distinguished simply by mass spectrometric detection methods. The large geometry change upon ring-opening is likely to ensure that the products are formed with high levels of internal (vibrational) excitation. Indeed, the internal energy within the nascent ring-opened isomer(s) may well be sufficient to allow further isomerization, and even fragmentation. Without subsequent collisional relaxation, measurement and assignment of spectra of the ring-opened species are likely to be challenging.

Identifying a measurable that allows visualization of the early time dynamics is a challenge for experimental studies of photoinduced ring-opening. Hence the recent interest in substituted heterocycles carrying a “reporter” group whose spectral signature changes as the ring opens. Molecules like 2-thiophenone (Figure 1), for example, are well suited to study by ultrafast UV pump, broadband TRIR probe methods. As Figure 5a,f shows, the TRIR spectrum obtained following 267 nm photoexcitation of 2-thiophenone in acetonitrile displays an immediate parent bleach at $\sim 1685$ cm$^{-1}$ and a broad TA centered at $\sim 1510$ cm$^{-1}$; the “reporter”, the carbonyl vibration in 2-thiophenone, evolves into a ketene asymmetric stretch mode in the ring-opened product. The breadth of the latter feature, and its subsequent narrowing and shift to higher wavenumber, confirms prior expectations that the ring-opened product will be formed vibrationally excited and then relax (on a picosecond time scale) by coupling with the solvent bath. In this particular case, the decline in the amplitude of the parent bleach signal with increasing $t$ implies that $\sim 60\%$ of the photoexcited molecules ultimately ring-close again to reform 2-thiophenone.

Results from similar UV-pump, TRIR absorption studies of four other carbonyl-bearing heterocycles—2-(SH)-furanone (henceforth 2-furanone), N-methyl-2-pyridone, $\alpha$-pyrone, and coumarin—are shown in Figure S, along with their associated structures. The solvent in each case was acetonitrile. Relative to 2-thiophenone, the UV absorption spectrum of 2-furanone is
shifted to shorter wavelengths, and the data shown here were recorded following 225 nm excitation. Photoinduced depletion of the ground state (i.e., ring closed) parent is revealed by the bleach signals centered at ∼1745 and 1775 cm⁻¹ (Figure 5b) and the formation and subsequent vibrational relaxation of the ring-opened ketene is shown by the broad absorption that narrows and progressively shifts to an eventual center wavelength of ∼2145 cm⁻¹ (Figure 5g). Kinetic analysis of the time evolving bleach signals indicates that only ∼10% of the photoexcited species return to the S₀ state of 2-furanone.36 Again, these solution phase studies are consistent with ασ*-state mediated asymmetric ring expansion leading to the formation of ring-opened ketene products.

The electronic absorption spectrum of N-methyl-2-pyridone stretches to longer UV wavelengths than that of 2-thiophenone, and the displayed TRIR data were taken following excitation at 330 nm. Bleach features are again evident (Figure 5c), as is a developing absorption at ∼2120 cm⁻¹ (Figure 5h).37 However, the time scales are all much slower than in the cases of 2-thiophenone or 2-furanone; kinetic analyses return a parent excited state lifetime of ∼100 ps. Most (>90%) of the excited-state population returns to the parent S₀ state (i.e., N-methyl-2-pyridone is relatively photostable, like many N-containing heterocycles38,39). However, Figure 5c and 5h also shows that a small (≤10%) fraction of the photoexcited molecules react to form two ketenes, which are in equilibrium. The identity of these ketenes remains an open question. Initial analysis identified a prefulvenic CI between the S₁ and S₀ PESs with the C═O group out of the plane defined by the other five heavy atoms, encouraging suggestions that the ketene isomers arose via ring contraction,37 but our more recent calculations identify two energetically accessible CIs between the S₁ and S₀ PESs characterized by extended N—C(O) bond lengths.

The remaining panels in Figure 5 show TRIR spectra measured following excitation of α-pyrone and coumarin (1,2-benzopyrone) at, respectively, 310 and 330 nm.40 α-pyrone is another 6-membered heterocycle, but with an O atom adjacent to the carbonyl group; fusing α-pyrone with a benzene ring constitutes coumarin. Photoexcitation of α-pyrone yields the expected bleach signal in the carbonyl stretch region (Figure 5d), and an absorption that narrows and shifts to higher wavenumber (∼2120 cm⁻¹) with increasing τ (Figure 5i). Again, this is the signature of vibrationally excited ketene products that “cool” by coupling with the surrounding solvent. Tracking the early time bleach recovery in the case of α-pyrone suggests an initial quantum yield φ ∼ 0.68 for IC and reformation of the parent in its S₀ state (φ ∼ 0.60 when photoexciting at 267 nm41). The ketene feature reveals the presence of at least two isomers, and temperature-dependent studies show that these undergo further (thermally driven E → Z) isomerization processes that provide a (slower) route to eventual near-total recovery of the starting α-pyrone(S₀) population.41

Coumarin shows very different behavior. As Figure 5e shows, the parent S₀ molecule is reformed with essentially unit efficiency following excitation at 330 nm.40 Yet the two lowest energy conical intersections (CI-a and CI-b) between the S₁ and S₀ states of α-pyrone and coumarin have remarkably similar geometries. Both involve O—C(O) bond extension and loss of planarity; the torsion angle between the carbonyl and ketene moieties at CI-a in both cases is ∼35°; at CI-b it is ∼90°.40,42 PECs calculated along linearly interpolated internal coordinates linking the respective Franck–Condon regions (i.e., the geometries at which α-pyrone and coumarin are initially excited) and the respective CIs show no significant energy barriers to ring-opening. Intrinsic reaction coordinate analysis offers a rationale for the very different ring-opening probabilities. Such analyses, initialized at the CI-a and CI-b geometries, suggest that only CI-b in α-pyrone promotes ring-opening.40 However, such analyses also remind us that knowledge of the nuclear geometry at a CI is necessary but generally is not sufficient information to allow prediction of the nuclear dynamics. *Ab initio* molecular dynamics (AIMD) simulations are finding growing use for exploring nonadiabatic excited state dynamics,40,42,45 but applying such methods to systems like α-pyrone and coumarin is a challenge. In both cases, photoexcitation yields excited states with reported lifetimes in the psec range, which are likely to be subject to a range of nonadiabatic couplings with close-lying states both within the Franck–Condon region, and en route to and at CI-a and CI-b.40,42,45 AIMD simulations thus require use of suitably high level electronic structure methods, long propagation times and, eventually, proper inclusion of solvent effects. Our work to date,
being just the isolated molecules, suggests that only in the case of Cl-b in α-pyrones are the out-of-plane momenta sufficient to enable asymptotic ring-opening.

Knowledge of the nuclear geometry at a CI is necessary but generally is not sufficient information to allow prediction of the nuclear dynamics.

These solution phase studies provide clear evidence for the formation of ring-opened ketene products following near UV photoexcitation of α-pyrones. Electronic structure calculations imply the operation of a similar asymmetric ring expansion following near UV photoexcitation of coumarine but, in this case, the forces acting during nonadiabatic coupling in the region of Cl-a/b favor reformation of the ring-closed parent. Theory also reveals low energy Cls between the S1 and S0 PESs of N-methyl-2-pyridone characterized by N=C(O) bond separation such as could lead to ring-opening, but the structures of the (minor yield) of ketene products formed following near UV photoexcitation of this molecule remain to be established.

It is now instructive to consider the extent to which the parent → product correlations shown for thiophene (Figure 4b) apply to the heterocycles featured in Figure 5. Following π̃n → π excitation of 2-thiophenone or 2-furanone, efficient nonadiabatic coupling to the near-resonant π̃n* PES (via Cl-1) can direct population toward Cl-2, where it transfers to the S0 PES and eventual branches to either reform the ring-closed parent or form one or more ring-opened products. There must be a rival 1π̃σ* PES that facilitates extension of the other S−C(O−C) bond in each of these molecules, but in both cases, the rival 1π̃σ* PES will lie at higher energy and correlate with less stable ring-opened products. The other molecules featured in Figure 5 show several important photophysical differences. The photoprepared states of 2-thiophenone and 2-furanone have lifetimes shorter than the ~1 ps response time in the reported experiments, whereas the excited state lifetimes of α-pyrones and coumarine and of N-methyl-2-pyridone are in the few picoseconds and 100 ps ranges, respectively. Second, S−C(O) (O−C(O)) bond fission in 2-thiophenone or 2-furanone yields a biradical. One or more H atom migrations are then required en route to the experimentally observed ketenes, reminiscent of the thermal suprafacial/antarafacial [n + m]-sigmatropic shift reactions observed in many conjugated hydrocarbons. Ketene formation following photoinduced N−C(O) bond fission in N-methyl-2-pyridone or O−C(O) bond fission in α-pyrones or coumarine, by contrast, would simply require an electrocyclic rearrangement; the nuclei are appropriately configured from the outset. These latter reactions show parallels with the photoinduced ring-opening of various cyclic-hydrocarbons, the outcomes of which accord with the Woodward–Hoffmann rules. Such rules should be expected to extrapolate to, and describe, the photoinduced ring-opening of N-methyl-2-pyridine, α-pyrene, and coumarine also. Third, the first excited 1π̃σ* states in these latter molecules all lie at much lower energy than the corresponding 1π̃σ* state in 2-thiophenone or 2-furanone, i.e., the vertical energy separations between the lowest 1π̃σ* and 1π̃σ* states in the featured six-membered heterocycles are substantially larger. This will reduce the probability of (and sufficiently low excitation energies completely rule out) nonadiabatic coupling to the 1π̃σ* PES at the analogue of Cl-1 as a route to asymmetric ring expansion following long wavelength π̃n → π excitation of N-methyl-2-pyridone, α-pyrene, or coumarine.

This can also be illustrated with the help of schematic 4-electron orbital correlation diagrams such as that shown for α-pyrene in Figure 4c. The key orbitals in this case are the partially conjugated 2n (a*) orbital on the ring oxygen atom, a relatively low-lying excited π̃n* (a*) orbital, and the bonding σC−C(O)* a* (a*) orbitals localized on the extending bond. In this description, the S0 parent molecule has the configuration (a*)2 (a*)2. The 1π̃σ* state has configuration (a*)2 (a*)2 at planar geometries, but an appropriate combination of twisting and O−C(O) stretching motion provides an energetically feasible nonradiative route back to the S0 state and possible ketene formation in the event of full O−C(O) bond fission. Clearly, state labels like 1π̃σ* progressively lose their meaning as the molecule distorts from planarity. The 1π̃σ* state, with configuration (a*)2 (a*)2 σC−C(O)* a* (a*), lies higher in energy and, importantly, correlates with an excited state ring-opened species, as illustrated in Figure 4c. The ring-opening revealed in Figure 5h,i, following near UV photoexcitation of N-methyl-2-pyridone and α-pyrene, can thus most plausibly be rationalized in terms of nonradiative coupling between the S1 (predominantly 1π̃σ*) and S0 states at distorted, twisted geometries. Such behavior is reminiscent of that shown following π̃n → π excitation of 1,3-cyclohexadiene, for example, which undergoes a conrotatory ring-opening to form 1,3,5-hexatriene (vide infra) with an inherent stereochemistry that can be understood by means of an orbital energy and symmetry correlation diagram linking the reactant and product. Such orbital correlation concepts can be expected to account for the out-of-plane ring-opening in α-pyrones also. The present analysis thus does not exclude a role for “classic” 1π̃σ* state mediated N−C(O) bond fission in N-methyl-2-pyridone (and O−C(O) bond fission in α-pyrene and, plausibly, coumarine), at shorter excitation wavelengths, to electronically excited ring-opened products, but this has yet to be demonstrated.

For completeness, we note that many of these same ring-opening processes had been previously recognized via IR spectroscopy measurements following prolonged broadband UV irradiation of, for example, 2-thiophenone, 2-furanone, and α-pyrene in an inert matrix. The recent solution phase studies (and accompanying theory) give greater insight into the primary photochemistry, and the mechanisms and quantum yields of ring-opening, but still cannot claim to be a direct probe of the ring-opening dynamics. Gas phase studies, allied with appropriate theory, offer the means of getting yet closer to this “holy grail”.

Gas-Phase Studies of Photoinduced Ring-Opening. As noted earlier, the 193 nm PTS results for thiophene are consistent with 1π̃σ*-state mediated asymmetric ring expansion, nonadiabatic coupling to the S0 PES and subsequent unimolecular decay. Recent imaging studies of the products formed by near UV photolysis of 2-bromothiophene (shown in Figure 1) and 2-iodothiophene provide further circumstantial evidence for photoinduced ring-opening in (substituted) thiophenes. As Figure 6a shows, the image of the ground state Br atoms (detected by 2 + 1 REMPI) formed following ~265 nm photoexcitation of 2-bromothiophene reveals a quite sharply defined, anisotropic velocity distribution. These products arise via prompt C−Br bond fission. Figure 6b shows an image of the partner thiophenyl radicals formed at a similar photolysis wavelength, and detected by 118 nm VUV ionization.
Reassuringly, this image shows the same recoil anisotropy, and the high velocity edge of its profile is momentum matched with that of the Br atoms. Analysis of these data reveal additional details including, for example, that the quantum yield for forming spin–orbit excited Br atoms at these wavelengths is small and that the slower thiophenyl fragments are under-detected in Figure 6b as a result of (unintended but unavoidable) dissociative photoionization by the 118 nm probe laser pulse. In the present context, however, the corresponding data taken when exciting at ∼245 nm (Figures 6c and 6d) are most noteworthy. Despite the increase in photon energy, the Br atom and partner m/z 83 radical images are both much smaller, and isotropic. Companion electronic structure calculations suggest that this evolving behavior reflects the onset of a rival excited state decay pathway, involving σπ*-state mediated asymmetric S–C(Br) bond extension, nonadiabatic coupling to the S0 PES and formation of one or more excited ring-opened isomers with sufficient internal energy to exceed the energetic threshold for unimolecular decay and loss of a (slow) Br atom.

The oxygen-containing analogue of thiophene is furan. PTS studies of furan following excitation at 193 nm identified three fragmentation pathways (a radical channel giving C6H4 + HCO products, and two molecular channels yielding, respectively, C6H4 + CO and H2C=CO + C2H2). These observations, and the respective product energy disposals, were rationalized by invoking photinduced ring-opening and subsequent unimolecular decay of the ring-opened species, but it was several years before the ultrafast excited state decay dynamics following excitation at 200 nm were explored by time-resolved photoelectron spectroscopy (TRPES), and σπ*-state mediated asymmetric ring expansion identified as a nuclear distortion capable of driving nonadiabatic coupling to the S0 PES. As Figure 7a shows, the calculated PECs along this O–C elongation coordinate leading to CI-2 in (planar) furan are very similar to those for the analogous asymmetric expansion in thiophene (Figure 2c). As in thiophene, theory also identifies a rival CI in furan with a ring-puckered geometry, which could also promote IC to the S0 state. Ultrafast TRPES studies of furan suggest that the excited-state population formed by 200 nm photoexcitation returns to the S0 state within ∼100 fs, and accompanying molecular dynamics simulations suggest contributions from both IC pathways.

Other notable recent studies include a theoretical work proposing σ* ← π excitation as a driver for O–C bond fission (i.e., ring-opening) in a spiropyran, and an ab initio study of the excited state photophysics of a carbohydrate molecule (β-D-glucopyranose) that predicts both 1σπ*-state-mediated O–C bond fission (i.e., ring-opening) and 3σπ*-state-mediated fission of the pendant O–H bonds. The saturation of the carbohydrate molecule is attractive in the present context, as it greatly reduces the range of possible orbital promotions. It is tempting to suggest that similar σπ* ← n excitations could trigger O–C bond extension, IC to the S0 state, and the eventual fragmentation reported following 193 nm photoexcitation of the cyclic ethers oxetane and tetrahydrofuran. An early theoretical study of photoinduced ring-opening of oxirane also hinted at such a mechanism.

Pyrrole and 1,3-cyclopentadiene are isostructural with furan, but these unsaturated 5-membered cyclic systems show quite distinctive excited state photophysics. The near UV photochemistry of pyrrole is dominated by prompt N–H bond fission following excitation from the (π) HOMO to a σ* orbital localized on the N–H bond. TRPES studies at these near UV wavelengths return excited state lifetimes of ∼20 fs. Other excited states are accessed upon tuning to shorter wavelengths; these excited states decay more slowly, by nonadiabatic coupling to the 3σπ*-continuum and N–H bond fission, and by rival nonradiative decay pathways to the S0 PES and subsequent unimolecular decay. The latter processes are revealed via an increased yield of slow H atoms and of products other than H + pyrrolyl fragments. Theory identifies CIs involving both ring-puckered and asymmetric ring-expanded

Figure 6. Br atom and partner C6H4S (m/z 83) fragment images from photolysis of jet-cooled gas phase 2-bromothiophene molecules at ∼265 nm (a,b) and 245 nm (c,d). Data adapted from refs 51 and 52.

Figure 7. Calculated PECs for (a) the S0 and lowest excited singlet states of furan along an R_C=C ring-opening coordinate and (b) the S0 and lowest excited singlet (shown in red) and triplet (in blue) states of 1,3-cyclopentadiene along the corresponding R_C=C ring-opening coordinate. All ring atoms are constrained to lie in a plane, and solid and dashed lines are used to distinguish states of A' and A" symmetry, respectively. Further details are provided in the Supporting Information.
geometries, but these dissociation pathways involving heavy atom distortions struggle to compete with the ultrafast N–H bond fission process. The latter can be slowed by substituting a Me group in place of the H atom. Studies of N-methylpyrrole reveal formation of translationally excited Me products, on a hundreds of picoseconds time scale, when exciting at wavelengths in the range 240–250 nm (i.e., to the $^1\sigma\pi^*$-continuum). Tuning to shorter wavelengths, the excited state lifetime drops substantially, and the Me fragments display a slow, essentially “statistical” kinetic energy distribution. Such observations have been rationalized by invoking the onset of a rival fast population loss process (IC to the $S_0$ state driven by ring-puckering and/or asymmetric ring-expansion) and subsequent unimolecular decay. Excited-state photophysics similar to that for pyrrrole has been predicted for imidazole where, again, IC via CIs involving both ring-puckered and asymmetric ring-expanded geometries have been identified as potential competitors to N–H bond fission at higher excitation energies.

Unlike the O atom in furan or the N atom in pyrrole, the corresponding ($\sigma^p$-hybridized) C atom in 1,3-cyclopentadiene supports no $\pi$ electrons. As Figure 7b shows, the ring-opened biradical in this case associates with just one singlet PES (which correlates with the $S_0$ state of the ring closed molecule) and a repulsive triplet potential. The $^1\sigma\pi^*$ state correlates to an electronically excited state of the biradical, and cannot mediate nonadiabatic coupling to the $S_0$ PES by appropriate elongation of the C$\equiv$C bond. Rather, theory (AIMD simulations) and experiment (TRPES) both suggest that the ultrafast non-radiative decay following $\pi^* \rightarrow \pi$ excitation in 1,3-cyclopentadiene involves initial (in-plane) motion along the bond-alternation coordinate followed by out-of-plane torsional motion about the C$\equiv$C double bonds (reminiscent of the motions following $\pi^* \rightarrow \pi$ excitation of ethene) so as to access regions of CI with the $S_0$ PES. The eventual fate of the resulting highly vibrationally excited $S_0$ molecules in a collision-free gas phase experiment remains an open question.

The photoinduced ring-opening of 1,3-cyclohexadiene has been studied more extensively. As with 1,3-cyclopentadiene, near UV absorption results in population of a “bright” $^1\pi\sigma^*$ excited state. A recent TRPES study questions the previous consensus view that the very early time dynamics following photoexcitation involves nonadiabatic coupling to an optically dark (2A) state. Thereafter, however, there is little doubt that the topography of the excited state PES(s) encourages C$5$$\rightarrow$C$6$ bond extension and torsion around the C$\equiv$C double bonds, thereby priming the molecule for radiationless transfer though a CI with the $S_0$ PES, rather than by a rival $^1\pi\pi^*$/$S_0$ coupling enabled by suitable out-of-plane distortions. A $^1\sigma\pi^*_{\text{C=C}-\text{Me}}$-mediated bond fission is argued to play an important role in the ultrafast ring-opening of the S-membered heterocycles thiophene and furan, and analogues like 2-thiophenone, 2-furanone, and 2-bromo- and 2-iodothiophene, but the recently observed near UV photoinduced ring-opening of N-methyl-2-pyridone and $\alpha$-pyrone is more likely driven by nonadiabatic coupling at CIs between the $^1\pi\pi^*$ and $S_0$ PESs at nonplanar geometries. Comparisons between $\alpha$-pyrone and coumarin serve to emphasize the importance of both structure and dynamics in determining the nonadiabatic coupling probability at any given CI, and to highlight the challenges of realistic dynamical calculations involving such systems. N-methyl-2-pyridone, $\alpha$-pyrone, and coumarin must possess $^1\pi\pi^*_{\text{C=C}-\text{Me}}$ ($X = N, O$) states, but these will typically lie at higher energies than have been investigated to date. The $^1\pi\pi^*$ states in these latter heterocycles all correlate with an excited state of the ring-opened species, so ring-opening may not be an exergic option following near UV photoexcitation. Such energetic constraints are likely to fade in importance on tuning to shorter (vacuum) UV excitation wavelengths, however, where electron promotions to the appropriate bond localized $\sigma^*$ orbital (and from bond localized $\pi$ orbitals) are both likely to exhibit progressively larger partial absorption cross sections.

Apart from its intrinsic photophysical interest, 1,3-cyclohexadiene has also been a popular test system for demonstrating new experimental routes for probing the dynamics of photoinduced ring-opening. The works cited at the end of the previous section include early examples of ultrafast condensed phase pump–probe studies, ultrfast transient ionization studies, TRPES and femtosecond X-ray spectroscopy studies, all of which either have been, or soon can be expected to be, applied to the various types of asymmetric ring expansion and heterocyclic ring-opening featured in this Perspective. To this growing armory of techniques, one can also anticipate growing interest in the use of Coulomb explosion imaging methods. Correlations and/or covariances revealed using such methods have already been shown to offer a direct probe of the photoinduced torsional dynamics of strategically substituted biphenyl derivatives on their ground-state PESs and are now starting to find use in probing photoisomerizations and excited state bond fission processes.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.7b01219.

Details of the calculation of potential energy profiles for the ground and various excited states of dimethylsulfide, thioanisole, thiophene, furan, and 1,3-cyclopentadiene along the chosen bond extension coordinate ($R_i$); Figure S data, displayed on an expanded scale and with the various time delays specified (PDF).

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