Unravelling the Keto-Enol Tautomer Dependent Photochemistry and Degradation Pathways of the Protonated UVA Filter Avobenzone

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Abstract

Avobenzone (AB) is a widely used UVA filter known to undergo irreversible photodegradation. Here, we investigate the detailed pathways by which AB photodegrades by applying UV laser-interfaced mass spectrometry to protonated AB ions. Gas-phase infrared multiple-photon dissociation (IRMPD) spectra obtained with the free electron laser for infrared experiments, FELIX, (600-1800 cm\(^{-1}\)) are also presented to confirm the geometric structures. The UV gas-phase absorption spectrum (2.5-5 eV) of protonated AB contains bands that correspond to selective excitation of either the enol or diketo forms, allowing us to probe the resulting, tautomer-dependent photochemistry. Numerous photofragments (i.e. photodegradants) are directly identified for the first time, with m/z 135 and 161 dominating, and m/z 146 and 177 also appearing prominently. Analysis of the production spectra of these photofragments reveals that strong enol to keto photoisomerism is occurring, and that protonation significantly disrupts the stability of the enol (UVA active) tautomer. Close comparison of fragment ion yields with the TDDFT-calculated absorption spectra give detailed information on the location and identity of the dissociative excited state surfaces, and thus provide new insight into the photodegradation pathways of avobenzone, and photoisomerisation of the wider class of \(\beta\)-diketone containing molecules.

Keywords

Photoisomerism, Sunscreen, Photodegradants, Laser Spectroscopy, \(\beta\)-diketone.
1. Introduction

In order that the skin can be protected against radiation damage linked to sunlight exposure, considerable effort has been put into the development of effective sunscreens. Over recent years, a number of advanced laser spectroscopic studies have been conducted on sunscreen molecules under highly-controlled conditions, with the aim of improving our fundamental knowledge of the mechanisms by which molecular sunscreens function. Such measurements aim to provide fundamental insights into the properties of the sunscreen molecule free from the complications of the complex environment of a real sunscreen lotion. One group of experiments has focused on “isolated” gas-phase sunscreen molecules to provide information on how UV light absorption varies as a function of molecular structure. A second group of studies have used transient absorption spectroscopy to probe relaxation dynamics of two-component mixtures of a single organic sunscreen molecule in a single solvent. Experiments are typically complemented by high-level quantum chemical calculations, which then provide important insights into the mechanism by which the sunscreen molecule operates.

**Scheme 1:** Schematic diagram illustrating the UVA active chelated-enol (CE) and UVB active diketo (DK) tautomer of avobenzone. Irradiation of the DK tautomer causes photo-initiated α-cleavage.

Avobenzone (AB: 4-tert-butyl-4’-methoxydibenzoylmethane; BD-DBM or Parsol 1789) is a widely used UVA filter which is known to suffer from irreversible UV-driven photodegradation. AB is a dibenzoylmethane derivative and a member of a family of molecules known to take multiple
isomerization pathways following UV excitation.\textsuperscript{25-30} Photoexcitation of AB is believed to lead to non-adiabatic population of high-lying $S_0$ vibrational levels, which can lead to isomerization to a less photostable form.\textsuperscript{31} Previous photolysis experiments performed in hexane have shown that this photodegradation of AB occurs by a Norrish type 1 mechanism.\textsuperscript{32-33} (The key tautomeric forms of AB involved in this photoisomerization are illustrated in Scheme 1.) In the ground state, AB is mostly found in its chelated enol (CE) form due to the stabilizing intramolecular hydrogen bond, although the diketo (DK) form is also typically present, with the relative tautomeric ratios being strongly solvent dependent. The CE form is the active UVA blocker ($\lambda_{\text{max}} = 355$ nm), with photoisomerization leading to non-chelate forms, which gradually populate the DK form. The DK tautomer absorbs at higher UV energies ($\lambda_{\text{max}} = 265$ nm) and has been shown to be responsible for formation of a reactive triplet. Indeed, the instability of the diketo form is well established.\textsuperscript{32,34-36} Wang et al., for example, demonstrated that AB photodegrades (in the UVA) more quickly as a function of chlorine substitution at the $\alpha$-carbon (C2) since this promotes the diketo form.\textsuperscript{37}

A considerable number of studies have been performed to explore how AB tautomerization, and hence photostability, is affected by the solvent.\textsuperscript{38-40} These studies prompt questions of whether other local environmental factors can influence the extent of tautomerization. In this work, we directly address one such issue, namely the potential effect of acid conditions on the photochemistry of AB by directly studying the protonated form of AB, i.e. AB-H\textsuperscript{+}, as an isolated system in the gas phase. We use laser-interfaced mass spectrometry (LIMS) to select ions that are then subjected to wavelength-dependent laser photodissociation, allowing us to measure the gas-phase absorption spectrum.\textsuperscript{41-42} LIMS has recently been shown to be a useful tool for studying isomeric systems.\textsuperscript{43-47} Applying LIMS to AB-H\textsuperscript{+} allows us to selectively investigate the photochemistry of both enol and keto tautomers, and to probe the extent to which tautomerization occurs, away from any influences of the bulk-phase environment. Importantly,
our experiments also allow us to measure the photodegradants of the individual AB·H⁺ tautomers. To complement the UV photochemistry, we present infrared multiple-photon dissociation (IRMPD) spectroscopy of AB·H⁺ to confirm which tautomers are present.

Fundamental studies of the effect of pH on sunscreen molecules to date are sparse. Recent measurements from our group have highlighted the impact of protonation and deprotonation on oxybenzone, in terms of the nature and wavelength dependence of its UV photofragmentation pathways. A separate study of deprotonated 2-phenylbenzimidazole-5-sulfonic acid provided direct evidence for the production of free radical photoproducts following UVA excitation. We note, however, that there is broad interest in the effect of pH in the field of environmental chemistry and degradation of man-made pollutants present in surface water, so that further work assessing the effect of pH on individual sunscreens is highly desirable.

2. Methods

Gas-phase UV photodissociation experiments were conducted in an AmaZon SL dual funnel electrospray ionization quadrupole ion trap (ESI-QIT) mass spectrometer (Bruker Daltonics Inc., Billerica, MA, USA), which was modified to allow LIMS. Avobenzone (AB) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and HPLC-grade EtOH was purchased from Fisher Scientific, Inc. (Pittsburgh, PA, USA), both used as received. Solutions of AB (1 × 10⁻⁴ mol dm⁻³) in EtOH were electrosprayed using typical instrumental parameters (nebulizing gas pressure of 10.0 psi; injection rate of 0.33 mL/h; drying gas flow rate of 8.0 L/min), and run in positive ion mode at a capillary temperature of 100 °C. AB·H⁺ was mass selected and isolated in the ion-trap prior to laser irradiation. UV-Vis photons were produced by a 10 Hz Nd:YAG (Surelite™, Amplitude Laser Group, San Jose, CA, USA) pumped OPO
(Horizon™, Amplitude Laser Group) laser, giving ~0.3 mJ across the range 400–216 nm (3.10–5.80 eV).

A 2 nm laser step size was used to record the photodepletion and photofragment spectra of the AB·H⁺ parent ion. To check for single-photon conditions, the laser power dependence on signal was determined as described previously.⁴²

Photofragmentation experiments were conducted with an ion accumulation time of 20 ms and a fragmentation time of 100 ms, thereby ensuring that each mass-selected ion packet interacted with one laser pulse, minimizing the likelihood of multiphoton events. When fluorescence is negligible,⁵⁸ the UV excited gaseous ion will fragment upon excited state relaxation, yielding an action absorption spectrum by photodepletion (PD).⁵⁷,⁵⁹-⁶⁰ PD was measured as a function of the scanned wavelength, with the photofragment production (PF) also recorded simultaneously at each wavelength, both of which according to:

\[
\text{Photodepletion Intensity} = \frac{\text{Int}^{\text{OFF}}}{\text{Int}^{\text{ON}}} \times \frac{\lambda}{P} \quad [1]
\]

\[
\text{Photofragmentation Intensity} = \frac{\text{Int}^{\text{FRAG}}}{\text{Int}^{\text{OFF}}} \times \frac{\lambda}{P} \quad [2]
\]

where \(\text{Int}^{\text{OFF}}\) and \(\text{Int}^{\text{ON}}\) are the peak intensities with laser off and on respectively; \(\text{Int}^{\text{FRAG}}\) is the selected fragment intensity with the laser on; \(\lambda\) is the excitation wavelength (nm); and \(P\) is the tunable laser pulse energy (mJ). The photodepletion intensities were taken from an average of three runs at each wavelength of the ranges studied. We note that fragment ions with \(m/z < 50\) are not detectable in our mass spectrometer because of the low-mass cut-off of the quadrupole ion trap. The UV photodepletion (absorption) spectra of the major AB photofragments produced upon the photoexcitation of AB·H⁺ were also recorded using MSⁿ scheme and mass-isolation feature available on the trapControl version 7.2 (Bruker Daltonics Inc.) software.
IR experiments were performed in a modified commercial quadrupole ion-trap mass spectrometer (Bruker, AmaZon Speed ETD). Ions were generated in an Apollo ESI source. Solutions of AB·H⁺ (1 × 10⁻⁶ mol dm⁻³) in MeOH were introduced at 180 µL/h flow rates, electrosprayed and transferred into the trap. The ions of interest were mass-selected and fragmented by IRMPD. IR spectra in the 700-1800 cm⁻¹ region were recorded using the FELIX infrared free electron laser. FELIX was set to produce IR radiation in the form of 5-10 µs macropulses of 80-120 mJ per pulse at a 10 Hz repetition rate and with a bandwidth of ~0.4% of the centre frequency. The mass-selected ions were irradiated with one macropulse. Resonant absorption of IR radiation leads to an increase of the internal energy of an ion mediated by intramolecular vibrational redistribution (IVR), which eventually leads to unimolecular dissociation. After irradiation, a mass spectrum of the resulting ions in the trap is recorded. At each IR frequency point, 6 mass spectra were averaged. The dissociation was calculated from the mass spectra by relating the precursor ion and fragment ion intensities (Equation 3) and plotted as a function of IR frequency.

\[
\text{IRMPD} = -\ln \left( \frac{\text{Int}_{\text{PRECURSOR}}}{\sum \text{Int}_{\text{PRECURSOR}} + \sum \text{Int}_{\text{FRAG}}} \right)
\]

The IRMPD intensity was linearly corrected for frequency-dependent laser pulse energy. Spectra were also recorded at two levels of laser-pulse energy attenuation (factors of 2.00 and 3.16) to prevent excessive depletion of the precursor ions (saturation) and minimize formation of low m/z fragment ions which may be undetected in the ion trap and which would result in underestimated IRMPD intensities. Calculations were performed using density functional theory in Gaussian 09. All reported structures correspond to true minima, as confirmed by frequency calculations. Conformational molecular dynamics searches implemented by Schrodinger’s MacroModel were conducted with mixed Monte Carlo torsional and low-mode sampling to generate possible conformers which were rapidly energy gradient minimized with the OPLS3e force field. Unique structures (RMSD 0.4 Å, < 100 kJ/mol) were then energy
minimized at the oB97XD/def2-SVP and M06-2X/def2-SVP levels of theory. An implicit solvent model was used to calculate the relative energies of conformers upon solvation. Frequency calculations at the B3LYP/def2-TZVPP level were performed to test that optimized structures are true minima and were used to interpret the IRMPD spectra.\textsuperscript{68}

3. Results

3.1 Quantum chemical calculations of gas-phase and solution-phase $AB\cdot H^+$

Scheme 2: Schematic diagram of the key tautomeric structures of $AB\cdot H^+$ with atom and rotation coordinate labels. The Ka ketone and Ea enol tautomers are protonated at the O2 atom, the Kb ketone and the Eb enol at the O1 atom.
Scheme 2 illustrates the key tautomeric structures of AB·H⁺. The atomic numbering system previously used by Kojic et al. is also followed here. The carbonyl group is the primary protonation site, although a natural population analysis of the low-energy structures indicates that the excess charge is delocalized (Section S1). A conformational molecular dynamics search was conducted on AB·H⁺, with the proton located on either the O1 or O2 site, followed by DFT optimization. Table 1 displays the tautomer relative energies, in the gas-phase and solution (rotamers are omitted from Table 1 as their electronic spectra are expected to be identical at our experimental resolution). The results presented in Table 1 suggest that solvation has little effect on the relative tautomer energies. We note that for the Kb structure, it was challenging to identify the minimum, which was only observed in the presence of solvent at the ωB97XD level of theory. The calculated relative energies for the various AB·H⁺ tautomers lead us to predict that the Ka isomer will dominate, both in the gas phase and in ethanol solution, with the Ea isomer also being present at a much reduced but still significant level.

Table 1. Calculated relative energies of AB·H⁺ and population analysis. Values in parentheses were calculated in ethanol solvent. NM = no minima found.

| Structure | Relative Energy (kJ mol⁻¹) | Population (%) |
|-----------|----------------------------|----------------|
|           | ωB97XD | M06-2X | B3LYP | ωB97XD | M06-2X | B3LYP |
| Ka        | 0 (0)  | 0 (0)  | 0     | 99 (77) | 75 (83) | 84 (91) |
| Kb        | NM (4) | NM (NM)| NM (NM) | NM (23) | NM (NM) | NM (NM) |
| Ea        | 16 (17)| 4 (6)  | 8 (11) | < 1 (< 1)| 20 (12) | 11 (6)  |
| Eb        | 20 (20)| 9 (9)  | 12 (13)|        | 4 (5)   | 4 (3)   |

*Relative electronic energy values are zero-point energy corrected.

Boltzmann probability distribution calculated at 100 °C from relative energy difference column values.
The lowest-energy isomers, Ka and Kb, are planar across the aromatic and diketone moieties. Suffixes a and b identify tautomer protonation site as O2 and O1, respectively, and this nomenclature is applied to the enol-like structures as well. The Ea structure represents the protonated enol form of AB·H+, which is non-planar, with the O1H1 bond (H1/O1/C1/R11) directed +10° out-of-plane and the R1-arene by −30° (O1/C1/R11/R12). The Eb structure is similarly non-planar with the O2H2 bond (H2/O2/C3/R21) positioned +12° and the R2-arene by −26° (O2/C3/R21/R22). The Ka and Ea tautomer energies vary significantly with different functionals, with ωB97XD placing Ea substantially higher in energy than when using M06-2X. This disagreement mirrors the previous reported issues in predicting relative energies values for the neutral keto and enol tautomers of dibenzoylmethane systems without anharmonic methods.27,69 Many of these previous papers also identified twisted Z and E rotamer geometries. Our conformational search identified many such twisted forms, but their relative energies lay at much higher energies (> 40 kJ/mol and 30 kJ/mol using the ωB97XD and M06-2X functionals, respectively) so they have been omitted from this work. The high energy of the twisted geometries highlights the electronic stability of the planar, hyper conjugated, AB·H+ ion.

**Figure 1:** Coordinate energy scans about the O2-H bond, presented with selected molecular structures.
As noted above, the Kb isomer only exists as a geometric minimum when optimized using the ωB97XD functional and with solvent present. Figure 1 shows the relaxed coordinate scan between Ka and Kb proton transfer geometries as a function of the O2H bond distance from 1.05 to 1.50 Å (a relaxed energy minimization at the ωB97XD/Def2-SVP level was performed at each scan coordinate). The calculated intermolecular hydrogen bond length is 1.41 and 1.46 Å in the gas phase and in ethanol, respectively. Our calculations reveal that while a 4 kJ/mol energy difference exists between the proton transfer isomers there is no barrier to this reaction in the absence of solvent. In ethanol, there exists a very small 1 kJ/mol barrier to the shallow potential well. Nonetheless, the Kb isomer exists by way of a motional resonance with Ka due to the in-plane intermolecular hydrogen bond. A symmetric C2/O2/H in-plane bend (Section S1) defines the Kb ← Ka proton migration and has a zero-point energy of 0.28 eV.

TD-DFT calculations were performed to determine the electronic excitations of the Ka, Ea and Eb structures. The resulting simulated electronic spectra are presented in Figure 2 for excitation energies between 2.5 and 6.0 eV and reveal that the absorption spectra associated with the low-energy cis structures, Ka and Ea/Eb, are quite different. The same was observed previously in experiments on neutral AB, and is directly related to the substantial change of electron density within the pseudocyclic moiety that occurs upon keto-enol tautomerisation. Three calculated spectra are overlaid for each isomer to explore the effect of changing functional. The Ka spectrum shows good agreement between the different dispersive functional treatments, while the PB0 spectrum is red shifted by 0.2 eV. The convolved spectral shape of Ka is nearly identical for all functionals chosen here, with each calculation predicting a strong transition followed by a medium strength transition 0.5 eV higher in energy. The Ea spectral profile is also similar for each of the dispersive functionals, with the PB0 spectrum red shifted by 0.26 eV. The convolved spectral shape of Ea shows two well-separated transitions, with the most intense being the lower-energy transition. Similar results were obtained for the
**Eb** tautomer, with the spectrum being red shifted by 0.06 eV compared to **Ea**. The difference between the most intense **Ka** and **Ea** transitions is 0.76 eV.

**Figure 2:** Calculated gas-phase TD-DFT excitation energies and simulated electronic absorption spectra (oB97XD, M06-2X, PB0) for **Ka**, **Ea**, and **Eb**. Oscillator strengths of individual transitions are given as vertical bars, while the full line spectrum is a convolution of the calculated transitions with a Gaussian function (0.5 eV FWHM). Excitation energies are presented unshifted.

### 3.2 IRMPD spectroscopy of **AB·H⁺**

Figure 3 shows the IRMPD total ion yield spectra of **AB·H⁺** (summed from yield spectra of photofragments at m/z 135 and 161 (major) and m/z 177 (minor) and m/z 255 (minor)), overlaid with the calculated vibrational spectrum of **Ka**, **Ea**, and **Eb**. The **Ka** species is predicted to have a dominant vibrational band at 1420 cm⁻¹. A strong (saturated) vibrational feature is evident in the experimental spectra in this region, consistent with **Ka** being present in the experimental ion ensemble. For the **Ea/Eb**
tautomers, the dominant vibrational band over the scanned spectral region is predicted to occur at 1562-5 cm\(^{-1}\). We assign the experimental feature at 1575 cm\(^{-1}\) (saturated) to this Ea/Eb tautomer vibration. The experimental spectrum is therefore consistent with both Ka and Ea/Eb tautomers being present in the electrospray ion ensemble, as predicted by the \textit{ab initio} population analysis reported in Section 3.1. The spectral features that occur across the 1100-1350 cm\(^{-1}\) region could be attributed to either keto or enol tautomers and so are not discussed in detail here. A series of composite calculated Ka and Ea infrared spectra (Section S2) support our assignment of the IRMPD spectrum as arising from a combination of Ka and Ea/Eb tautomers.

![Figure 3: IRMPD Spectrum of AB\(\cdot\)H\(^{+}\) (in pink) is shown overlaid with simulated spectra (in black) for (a) Ka, (b) Ea, and (c) Eb. The calculated frequencies are scaled by 0.97.](image-url)
### 3.3 Gas-phase UV absorption spectrum of $AB\cdot H^+$

Figure 4a displays the gas-phase absorption photodepletion spectra of $AB\cdot H^+$ (m/z 311) over the range 2.5-5.7 eV. There are two distinct bands, labeled I and II, with $\lambda_{\text{max}}$ values at 2.9 and 3.6 eV, respectively. We note that the falling edge of band I contains a minor shoulder which is likely to be an experimental artifact caused by an OPO crystal changeover at that energy. Band II is asymmetric with an extended shoulder to higher energies. The photodepletion spectrum was recorded under single-photon absorption conditions, confirmed by power studies at the $\lambda_{\text{max}}$ of bands I and II (Section S3).

**Figure 4:** (a) Gas-phase photodepletion spectrum of $AB\cdot H^+$. The solid line is a 5-point adjacent average of the data points. (b) Composite TD-DFT curves for $K_a$, $E_a$, $E_b$ at the $\omega$B97XD/def2-SVP level. The TD-DFT calculated electronic transitions have been red-shifted by 0.53 eV, \(^7\) and intensities weighted by the Boltzmann populations.
The main features of the experimental photodepletion spectrum can be well reproduced by the calculated gas-phase absorption spectrum (Figure 4b), which sums the TD-DFT spectra of the Ka, Ea, and Eb isomers (Section 3.1). (The contributions of each isomer are scaled to match the calculated gas-phase Boltzmann populations (Table 1) and the calculated electronic transitions have been red shifted by 0.53 eV to match the observed experimental band positions). This allows confident assignment of band I to the bright S\textsubscript{1} transitions of the Ea/Eb pair of isomers, and band II to bright S\textsubscript{1} and S\textsubscript{3} transitions of the Ka isomer (note that depending on the functional used there are minor contributions from weak transitions within band II and small differences in the ordering of states S\textsubscript{1}-S\textsubscript{4}).

\textbf{3.4 UV Photofragmentation of AB·H\textsuperscript{+}}

Figure 5 displays the photofragment difference mass spectra of AB·H\textsuperscript{+} photoexcited at the band I and II maxima (2.6 and 3.6 eV, respectively). The dominant photofragments observed are m/z 161 [4a] and m/z 135 [4b], with both being products of McLafferty-like retro-heteroene hydrogen rearrangements adjacent to the a and b protonation centers.71

\begin{align*}
\text{AB·H}^+ + h\nu &\rightarrow \text{C}_9\text{H}_{10}\text{O}_2 + m/z 161 \quad [4a] \\
&\rightarrow \text{C}_{14}\text{H}_8 + m/z 135 \quad [4b]
\end{align*}

In addition to the hydrogen rearrangement products, several minor photofragments are produced across all probed wavelengths. Two of the more prominent minor photofragments are m/z 146 [4c] and m/z 177 [4d].

\begin{align*}
\text{AB·H}^+ + h\nu &\rightarrow \text{C}_{10}\text{H}_{14} + \text{CH}_3\text{O}^* + m/z 146 \quad [4c] \\
&\rightarrow \text{C}_{10}\text{H}_{14} + m/z 177 \quad [4d]
\end{align*}
These photoproducts arise from proton transfer from a carbonyl to a ring group, with subsequent elimination of neutral molecules. The m/z 146 fragment is an unusual odd-electron photofragment, which is not produced in CID of AB·H$^+$ (Section S4). This is a notable observation since this fragment, and the accompanying free radical(s), are therefore produced from AB·H$^+$ following UVA excitation only. Table 2 presents proposed structural assignments of the major observed AB·H$^+$ photofragment ions, as well as those produced by thermal fragmentation (CID; Section S4). Additional minor fragmentation channels are tabulated in Section S4.

**Figure 5**: Photofragment difference (laser on − laser off) mass spectrum of AB·H$^+$ excited at (a) 2.9 eV, and (b) 3.6 eV. *represents the depleted parent ion signal at m/z 311.
**Table 2.** Proposed structures for the major ionic and associated neutral fragments of AB-H⁺ (m/z 311) produced during CID and UV laser photoexcitation.

| Fragment Mass (m/z) | Proposed Structure of Fragment | m/z lost from AB-H⁺ | Fragment Results from Loss of Neutral | Observed in CID a,b | Observed in UV Laser Photoexcitation a |
|---------------------|--------------------------------|---------------------|--------------------------------------|---------------------|----------------------------------------|
| 255                 | ![Proposed Structure](image)   | 56                  | ✓ (m)                                | ✓ (w)               |                                        |
| 177                 | ![Proposed Structure](image)   | 134                 | ✓ (m)                                | ✓ (w)               |                                        |
| 161                 | ![Proposed Structure](image)   | 150                 | ✓ (s)                                | ✓ (s)               |                                        |
| 146                 | ![Proposed Structure](image)   | 134+31              | ✓ (w)                                |                     |                                        |
| 135                 | ![Proposed Structure](image)   | 176                 | ✓ (s)                                | ✓ (vs)              |                                        |

a very strong (vs), strong (s), medium (m), and weak (w). b The IRMPD photofragments are identical to the CID fragments listed here and have similar relative intensities.

To determine whether any of the observed photofragments arise from secondary fragmentation, the major photofragment ions m/z 161 and m/z 135 were isolated in the ion trap and then subjected to
photoexcitation. The resulting photofragment action spectra are displayed in Section S5 and reveal that neither m/z 161 nor m/z 135 directly photofragment to produce any other observed photofragments.

**Figure 6:** Relative ion yield plots for (a) the m/z 161, 135, (b) m/z 146, 177 photofragments of AB·H⁺ between 2.6-5.5 eV, and (c) the TD-DFT calculated excitation energies for each isomer at the ωB97XD/def2-SVP level. The curved lines included with the data points are a five-point adjacent average of such data points. Calculated excitation energies have been red shifted by 0.53 eV.
Figure 6 displays a plot of the wavelength-dependent relative ion yields of the key AB·H\(^+\) photofragments, providing a concise overview of the photofragment branching ratios. Full photofragment action spectra are included in Section S5. At the maxima of band I (2.9 eV) the major fragment ions m/z 161 and m/z 135 appear in equal proportions with each accounting for roughly 32% of the total photofragmentation signal. The onset of band II (3.3 eV) sees an increase in the relative ion intensity of m/z 135, with peaks in production of this ion at 3.4 and 4.3 eV (where it constitutes 50% and 60% of the total photofragmentation, respectively). The relative intensity of the m/z 161 photofragment falls to 25% at these energies. At photon energies above 4.8 eV, the relative ion intensities of the m/z 161 and m/z 135 pair of photofragments are again approximately equal, with the total branching into these fragments being slightly higher than in the band I region.

The m/z 146 fragment is produced most intensely in the low-energy spectral region between 2.7 and 3.6 eV, with its relative intensity decreasing across the band I region from 8% to 3%, and with a small enhancement in production around 4.5 eV. The m/z 177 ion is similar across the band I region, with respect to m/z 146 spectrum. Between 4.5 and 5.2 eV, the relative ion intensity of m/z 177 increases dramatically, peaking strongly around 4.7 eV. Notably, this peak in production of m/z 177 does not follow the same profile as band II of the photodepletion spectra, but does coincide with a pair of predicted weak \(E_a\) and \(E_b\) excitations at 4.8 and 4.9 eV (Figure 6c).

Approximately 15-20% parent ion depletion (I\(_{\text{off}}\)-I\(_{\text{on}}\)) is not recovered as measurable photofragmentation signal, an effect that can be attributed to production of ion fragments with m/z < 50 which is below the instrumental low mass cut-off. For example, heterolytic dissociation of the R\(_2\)-bound methoxy group would produce an even-electron ion at m/z 31 along with zwitterionic C\(_{19}\)H\(_{20}\)O\(_2\).
Finally, it is useful to review the photofragments produced compared to those observed via CID. CID, like IRMPD, is equivalent to thermal-induced dissociation and produces so called statistical fragments. For AB·H⁺, CID produces m/z 161 and m/z 135 as the dominant ionic products (Figure S8), with approximately equal intensity. Notably, these are the major photofragments observed in this study. From the relative ion intensities shown in Figure 6, it is evident that production of the m/z 161 and m/z 135 pair of photofragments is broadly statistical in the regions from 2.7-3.2 eV (i.e. the band I region), and above 5 eV (i.e. above band II). However, in the region between 3.7 and 4.7 eV (Vis to near-UVA), photofragmentation is clearly non-statistical with production of the m/z 135 photofragment being photochemically enhanced.42,72-76

4. Discussion

4.1 Mechanisms of dissociation for the Ka and Ea/Eb isomers of protonated avobenzone

From the calculated TD-DFT spectra presented in Section 3.1, excitations associated with the Ka tautomer dominate in the region between 3.7-5.0 eV, while Ea/Eb excitations dominate for energies between 2.5-3.7 eV. One of the striking features of the ion yield production spectra is that production of the m/z 135 photofragment peaks strongly at 3.6 and 4.3 eV. These energies coincide with the calculated bright transitions for the Ka tautomer (Figure 6c), leading to the conclusion that enhanced production of the m/z 135 photofragment follows excitation of keto tautomer transitions. At the energies where production of m/z 135 is enhanced, the relative ion intensity of m/z 161 decreases, which is expected for a relative ion intensity plot (i.e. if one relative ion intensity increases, another ion intensity must decrease).
Scheme 3: Proposed McLafferty-like rearrangement to form products (4b, 4a).

Scheme 3 presents the proposed fragmentation pathways for the m/z 161 and m/z 135 fragments, associated with hydrogen rearrangement within the protonated diketo bridge of Ka. Since the odd-electron m/z 162 and m/z 136 photofragments are not observed, we can rule out direct α-cleavage of the Ka and Kb tautomers, as occurs for the corresponding neutral tautomers in solution. Instead, a retro-heteroene addition of the γ-hydrogen (charge carrier) to the Ka and Kb tautomers generates the m/z 135 and m/z 161 ions, respectively (Kb is included in this scheme, as it was established (Section 3.1) to be vibrationally populated by Ka). The Scheme 3 mechanism resembles the classic McLafferty rearrangement for ionic and radical molecules containing a keto group which undergoes β-cleavage. (For AB-H⁺, a protonated hetero atom occupies the saturated γ-carbon position typical to McLafferty systems.) Scheme 3 illustrates that the m/z 161 and m/z 135 fragments can be produced in a straightforward mechanism from a keto tautomer, but no similar McLafferty-like rearrangement can be deduced from an enol tautomer (the reduced C2 β-carbon of either Ea/Eb species needs an additional hydrogen for this reaction (as shown) to occur). Thus, Scheme 3 provides further evidence that m/z 161 and m/z 135 derive from a Ka/Kb tautomer.
Scheme 4: Proposed product formation from the AB·H+ enol tautomers by a) proton transfer preceding ring-walk and elimination [4d] and by b) homolytic fission of the R₂-methoxy bond prior to proton transfer preceding ring-walk and elimination [4c]. Dotted arrows indicate the proposed reaction path.

*m/z 280 is not detected.

The ion fragments m/z 177 and m/z 146 are photoproducts which can be assigned as being unique to the isomer Ea. The spectral profile traces of m/z 177 and m/z 146 shown in Figure 6b match the computed
spectra of \textbf{Ea}/\textbf{Eb} (Figure 6c). Scheme 4a presents a tentative mechanism for the formation of m/z 177 from \textbf{Ea} via a proton transfer from the enol to the nearby ring. Following this transfer a ring-walk and subsequent elimination yields the detected ion fragment. The proton transfer ring-walk mechanism proposed here is akin to those proposed previously for fragmentation patterns of elimination substitution (ortho, meta, para) of aromatic systems.\textsuperscript{81-83} An analogous mechanism from the \textbf{Eb} isomer (not shown) would yield the m/z 255 ion fragment which was measured with very low intensity and therefore omitted from Figure 6b. At the same time, the observation of the m/z 255 photofragment indicates that \textbf{Eb} is present at low concentration in our ion ensemble. Scheme 4b includes the homogeneous dissociation of the R\textsubscript{2}-methoxy group followed by a mechanism similar to 4a to yield m/z 146.

\textbf{4.2 Implied photodynamics of Ka and Ea/Eb conformers}

Previous work by Dunkelberger et al.\textsuperscript{25} on neutral AB in solution measured non-radiative formation of transient hot ground-state intermediates formed upon excitation of the CE form. These transients were found to be accessed by a series of largely rotational coordinate-driven conical intersections (CIs) in less than 1 ps, with the chelation of CE being broken by either out-of-plane OH motion, or C1-C2, C2-C3 centered dihedral (i.e. twisted) rotations. Solvent effects were found to influence the relaxation rates back to the CE equilibria, with the rotated OH form being the most rapid to equilibrate at $\tau = 1.3$ ps, while the twisted forms displayed tens of ps to $\mu$s-ms measured lifetimes. A CI was identified along the intramolecular proton transfer tautomerization coordinate which had a relaxation lifetime of 6 ps. Overall, these observations revealed that the rate of enol to keto tautomerization for the neutral in solution is low.
It is useful to consider how the known photodynamics of the neutral change upon protonation. From the discussion above, it is clear that pathways involving the OH group (i.e. out-of-plane OH rotation and tautomerization) play key roles in the decay dynamics. Protonation is highly likely to disrupt these pathways, since protonation of the carbonyl of the CO of the CE will lead to a decrease in the intramolecular hydrogen-bond strength.

Given that AB-H+ produces the m/z 135 and 161 photofragments across the Ea/Eb excitation wavelengths, and the fact that Ea/Eb structures cannot produce these product ions (Section 4.1), our results indicate that enol to keto photoisomerization AB-H+ must be occurring, followed by subsequent degradation into m/z 135 and 161. Even at the peak of Ea/Eb absorption (2.9 eV), 75% of the detected photofragments arise from keto structures. For neutral AB, enol to keto tautomerization has a very low cross-section from the measured rates. If we assume that the photofragment cross-section is directly proportional to the relaxation rates of the initially populated excited states into photoproducts, then our experiment suggests that the cross-section for dissociative excited-state decay observed for AB-H+ is substantially greater than for AB in solution. One explanation of this observation is that protonation lowers the energetic barriers to ‘twisting’ mechanisms that enhance enol to keto photoisomerization. High level computational potential energy scans of transition state geometries would be valuable to clarify this and solution-phase studies on the protonates species are clearly warranted.

This work has shown the protonation of the β-diketone bridge is responsible for a shift from type I to II photoelimination of AB. Neutral AB in solution is known to undergo Norris Type I (photo-initiated α-cleavage) dissociation and subsequent recombination. This dissociation process produces radical
fragments aided, in part, by the long-range repulsive force of an excited triplet spin-state.\textsuperscript{31} Norris Type II reactions, which are analogous to thermally-activated McLafferty rearrangements seen in mass spectrometry, rely on the acidic nature of excited states to access an $S_0 \leftrightarrow S_1/T_1$ CI by way of a downhill $\gamma$-hydrogen potential coordinate, widely known as excited-state intramolecular proton transfer.\textsuperscript{31,84-86} Whether the photodegradation of $\text{Ea}/\text{Eb}$ proceeds through an excited triplet state cannot be directly experimentally identified here. However, the observation of the m/z 146 photofragment (a free-radical fragment) is indicative of fragmentation via a triplet state.

Computational work on neutral AB by Kojić \textit{et al.} showed that under both gaseous and solvated conditions (MeCN), the $S_1$ state of $\text{CE}$ has a $T_1$ state of alternate spin parity available energetically within the zero-point-energy window of $S_1$ at the Frank-Condon geometry.\textsuperscript{27} If $T_1$ is accessed, there is a flat potential about the out-of-plane OH dihedral coordinate which crosses the contorted $S_0$ state. An easily accessible $T_1$ state for $\text{Ea}/\text{Eb}$ at $S_1$ Franck-Condon geometries may facilitate the rearrangements shown in Scheme 4. Future calculations of the excited state potential energy surfaces would be valuable to provide further insight into the photophysics.

\textbf{4. Concluding Remarks}

In summary, we have investigated the photochemistry of selected enol and keto isomers of protonated avobenzone in the gas phase. IRMPD spectroscopy was employed to confirm the presence of both enolic ($\text{Ea}/\text{Eb}$) and diketone ($\text{Ka}$) isomers of $\text{AB.H}^+$ in the electrosprayed ion ensemble. The dominant electronic excitations of the enol and keto tautomers of gaseous $\text{AB.H}^+$ were found to be well separated, allowing us to determine the tautomer-dependent photofragmentation products. Such measurements would be extremely challenging to perform in solution, due to the solution-phase tautomers displaying
overlapping spectral profiles. Analysis of the wavelength-dependent production of the various photofragments revealed that near-UVA photoexcitation provides a route to enol-to-keto tautomerization, consistent with previously proposed mechanisms for photodegradation of avobenzone in the condensed phase. Finally, we observed odd-electron photofragments in low quantum yield from the enol tautomer of AB-H⁺, which indicates that a previously unidentified photosensitizing pathway is present for this isomer. Prior studies of the neutral AB system have identified triplet excited states for the keto form.

We note that gas-phase photoisomerization has been studied by Bieske and co-workers, using ion mobility to detect photoisomers generated from protonated azobenzenes. Sheps and co-workers have performed an elegant series of experiments on gaseous neutral acetylacetone (a prototypical β-diketone), to probe keto to enol tautomerization using a combination of photoionization techniques. However, work presented here provides an important complement to these earlier studies since it demonstrates a method for directly detecting the photoproducts of a photoisomerizing system.

In the context of the current study of AB-H⁺, it is useful to compare the results to our previous work on protonated oxybenzone, OB-H⁺. Oxybenzone is another widely used UV sunscreen, and provides an interesting contrast to AB since it is known to exhibit excellent photostability. The OB-H⁺ contains a pseudocycle, formed by the intramolecular bond between the hydroxy and carbonyl groups. The McLafferty-like elimination reaction responsible for the most intense AB-H⁺ fragments cannot be produced straightforwardly from the enolic tautomers of AB-H⁺, or similarly, from OB-H⁺ due to the pseudocyclic nature of both structures. Moreover, while an enol-to-keto tautomerization in AB-H⁺ can lead to this elimination reaction, the direct conjugation of the pseudocycle and benzene ring in OB-H⁺
restricts this reaction pathway. Such comparative measurements are valuable for gaining a broader understanding of the molecular-level performance of different sunscreen molecules, and may be useful in the context of efforts to develop new sunscreen molecules.\textsuperscript{2,95}

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**Conflict of Interest**

The authors declare no conflict of interest.
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**SUPPLEMENTARY INFORMATION**

**Unravelling the Keto-Enol Tautomer Dependent Photochemistry and Degradation Pathways of the Protonated UVA Filter Avobenzone**

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**Supplementary Material**

S1 Additional DFT and TDDFT calculations

S2 Composite AB·H⁺ IR Ka and Ea spectra

S3 Photodepletion laser power dependence

S4 Collision induced dissociation measurements on AB·H⁺

S5 Additional photofragmentation measurements

S6 Possible heterolytic cleavage products of AB·H⁺ isomers
S1 Additional DFT and TDDFT calculations

Natural population analysis (NPA) results are shown for the optimized structures $K_a$, $E_a$, and $E_b$ at the ωB97XD/Def2-SVP level of theory in Figure S1.¹ NPA is a more accurate description of charge distribution than the Mulliken population analysis method but may overexaggerate charge distribution when compared to more robust electrostatic potential fit (ESP) methods.²⁻³

**Figure S1** Charge density plots from a natural population analysis (NPA) of $K_a$, $E_a$, and $E_b$.

The contrast scheme is scaled from -0.7 to 0.7 au.
The scaled vector representation of the OH\textsubscript{VIB} of Ka is shown in Figure S2 to elucidate the motional population of Kb. Kb was shown not to have a minimum optimized structure for the ground state at both ωB97XD/Def2-SVP and M06-2X/Def2-SVP levels of theory. The primary coordinate of this OH\textsubscript{VIB} can stretch to the approximate Kb geometry (Figure 1) at the expense of 0.04 eV (0.05 eV in ethanol) on a one-dimensional potential energy surface. The vibration shown in Figure S2 has a v(1) = 2294 cm\(^{-1}\) (0.28 eV), calculated at the ωB97XD/Def2-SVP level. Using the harmonic approximation:\textsuperscript{4-5}

\[
ZPE = \frac{1}{2} \sum_{i=1}^{3N/6} \nu_i
\]

For the vibration Figure S2, the ZPE of the mode is therefore 1150 cm\(^{-1}\) (0.14 eV) which is adequate energy to motionally activate the Kb structure from Ka.

**Figure S2** Scaled vector representation of OH\textsubscript{Vibration} for Ka isomer of AB-H\(^+\).
The interpretation of a gas-phase spectroscopic study for compounds typically used in the condensed phase (e.g. sunscreens in a cosmetic solution) require some brief notes on the chromatic effects with respect to phase. Additionally, the primary goal of measuring AB-H\(^{+}\) with photodepletion and photofragmentation spectra was to assess the photochemistry of the minor bulk components of AB (i.e. protonated species produced through acidification or equilibrium distribution of which the concentration is pH dependent). Protonation is expected to lead to chromatic effects as well. Figure S3 presents TD-DFT calculated electronic spectra of AB-H\(^{+}\) and AB at the ωB97XD/Def2-SVP level, in gaseous and ethanol conditions. Overlaid with the gas-phase AB-H\(^{+}\) calculations is the photodepletion data (light blue) from this study and overlaid with the solution phase AB calculations is an experimental UV-VIS taken of AB (1 \times 10^{-5}\text{ M}) in ethanol. A 0.53 eV red shift was applied to all the TD-DFT calculated spectra to give good agreement to experimental data. The TD-DFT spectra presented in Figure S3 have not been scaled to account for relative energy derived Boltzmann distributions, and thus are not expected to match the experimental data with respect to peak intensities.

The calculations predict that for most of the AB and AB-H\(^{+}\) tautomers, a blue shift occurs for the excitations on moving from solvent (ethanol) to the gas phase, with an average blue shift of 0.17 eV for individual excitations. The exception is for Ea\textsubscript{EtOH} \rightarrow Ea\textsubscript{GAS}, for AB and AB-H\(^{+}\) which display red shifts of 0.43 eV. Comparing the calculated AB and AB-H\(^{+}\) excitations, an average red-shift of 0.8 eV is observed for most of the tautomers, irrespective of solvation. However, on moving from the CE form of the neutral to the Ea tautomer of AB-H\(^{+}\), a blue-shift of 0.11 eV is seen. Overall, the calculated spectra are consistent with the experimental gaseous and solution-phase spectra, and thus provide direct insight into how protonation changes the electronic spectrum of AB in the gas-phase and in solution.
Figure S3 TD-DFT calculated electronic spectra of the gas-phase vs. solution (EtOH) spectra of AB and AB·H⁺. Calculations performed at the ωB97XD/Def2-SVP level and shifted by -0.53 eV to match the experimental data. The dashed lines represent shifts with respect to change between ethanol and the gas-phase (- • -), and from neutral to protonated (•••) AB.
A quantitative study was not performed by IRMPD for AB-H\(^+\) and the spectra were presented to identify only the presence of isomers. Traditionally, the IRMPD intensities would be compared to the theoretical calculations but the saturation observed in the experimental spectra above 1400 cm\(^{-1}\) makes this difficult. Additionally, there is the issue of variability of IRMPD spectral intensities discussed in full in a review by N. Pulfer.\(^6\) We present the calculated IR spectra for isomers Ka and Ea which were weighted to best match the experimental IRMPD spectra. Figures S4-S6 represent 45\% Ka, 50\% Ka, and 75\% Ka weightings, respectively.

**Figure S4** Composite AB-H\(^+\) IR calculated spectra (performed at the B3LYP/def2-TZVPP level) presented with the experimental IRMPD results for a 45\% Ka and 65\% Ea isomeric mix.
Figure S5 Composite AB-H⁺ IR calculated spectra (performed at the B3LYP/def2-TZVPP level) presented with the experimental IRMPD results for a 50% Ka and 50% Ea isomeric mix.
Figure S6 Composite AB-H⁺ IR calculated spectra (performed at the B3LYP/def2-TZVPP level) presented with the experimental IRMPD results for a 75% Ka and 25% Ea isomeric mix.
Photodepletion laser power dependence

Laser power measurements were conducted on AB·H⁺ at $E_a$ and $K_a \lambda_{\text{max}}$ photon energies, 2.9 and 3.6 eV respectively, to test for the presence of multiphoton effects. The plot displayed in Figures S7 shows the photodepletion intensities ($I_{\text{OFF}} - I_{\text{ON}}$) at these wavelengths. The data has been plotted on a log-log scale and fit to a power function. The resultant slope is proportional to the number of absorbed photons. The slopes at both photon energies measure less than 1. This result indicates that photodepletion is not multiphoton in nature. Additionally, this < 1 pseudolinear slope likely indicates saturation of the linear transition.

**Figure S7** Power dependent measurements for AB·H⁺ photodepletion at $K_a \lambda_{\text{max}}$ (3.6 eV) and $E_a \lambda_{\text{max}}$ (2.9 eV).
Collisional induced dissociation analysis of AB-H⁺

Low-energy collision induced dissociation (CID) was employed to determine the ground state thermal fragmentation products of AB-H⁺. This technique was performed by applying an excitation AC voltage to the end caps of the trap to induced collisions of the trapped ions with the He buffer gas, as also described in detail previously.³⁹ Figure S8 presents the relative intensities of AB-H⁺, and the corresponding fragment ions as a function of CID energy.

**Figure S8** CID fragmentation decay curve for AB-H⁺ (m/z 311) upon low energy CID. Onset plots for production of the associated fragment ions (a) m/z 161 and 135, and (b) m/z 293, 255, 237, 203, 177, 147, 109, 105, and 95 are also shown. The curved lines included with the data
points are a three-point adjacent average of the data points and are provided as a viewing guide,  to emphasize the profile for individual fragments.

Table S1. Proposed structures for the major ionic and associated neutral fragments of AB-H⁺ (m/z 311) produced during CID and UV laser photoexcitation.

| Fragment Mass (m/z) | Proposed Structure of Fragment | m/z lost from AB-H⁺ | Fragment Results from Loss of Neutral | Observed in CID * | Observed in Laser Photoexcitation * |
|---------------------|--------------------------------|---------------------|--------------------------------------|-------------------|-------------------------------------|
| 293                 | ![Proposed Structure](image)   | 18                  | H₂O                                  | ✓ (vw)            |                                    |
| 255                 | ![Proposed Structure](image)   | 56                  | ![Fragment](image)                  | ✓ (m)             | ✓ (w)                               |
| 237                 | ![Proposed Structure](image)   | 18+56               | H₂O                                  | ✓ (w)             |                                    |
| 203                 | ![Proposed Structure](image)   | 108 b               | ![Fragment](image)                  | ✓ (w)             |                                    |
| 177                 | ![Proposed Structure](image)   | 134                 | ![Fragment](image)                  | ✓ (m)             | ✓ (w)                               |
| 161 | ![Chemical Structure](image) | 150 | ![Chemical Structure](image) | ✔️ (s) | ✔️ (s) |
|-----|----------------------------|-----|----------------------------|--------|--------|
| 147 | ![Chemical Structure](image) | 56+10 | ![Chemical Structure](image) | ✔️ (w) | |
|     | ![Chemical Structure](image) | 8 | ![Chemical Structure](image) | ✔️ (w) | |
| 146 | ![Chemical Structure](image) | 134+3 | ![Chemical Structure](image) | ✔️ (w) | |
|     | ![Chemical Structure](image) | 1 | ![Chemical Structure](image) | ✔️ (w) | |
| 135 | ![Chemical Structure](image) | 176 | ![Chemical Structure](image) | ✔️ (s) | ✔️ (vs) |
|     | ![Chemical Structure](image) | | ![Chemical Structure](image) | | |
| 118 | ? | 193 | ? | ✔️ (vw) | |
| 109 | ? | 202 | ? | ✔️ (vw) | |
| 105 | ![Chemical Structure](image) | 206 | ? | ✔️ (vw) | ✔️ (vw) |
|     | ![Chemical Structure](image) | | ![Chemical Structure](image) | | |
| 95  | ![Chemical Structure](image) | 216 | ? | ✔️ (vw) | ✔️ (vw) |
|     | ![Chemical Structure](image) | | ![Chemical Structure](image) | | |
| 92  | ![Chemical Structure](image) | 219 | ? | ✔️ (w) | |
| 77  | ![Chemical Structure](image) | 234 | ? | ✔️ (w) | |

*very strong (vs), strong (s), medium (m), and weak (w). The IRMPD photofragments are identical to the CID fragments listed here and have similar relative intensities.*
S5 Additional photofragmentation measurements

Figures S9 and S10 show the photofragment production spectra of the major m/z 135 and 161 and minor m/z 77, 92, 105, 118, 146, 177, and 255 photofragments, respectively.

Figure S9 (a) Gas-phase photodepletion spectrum of AB·H⁺, (b-c) displayed with the photofragment production spectra of two major AB·H⁺ photofragments at m/z 135 and m/z 161, respectively. The solid line is a five-point adjacent average of the data points.
Figure S10 (a-h) Photofragment production spectra of eight minor photofragments of AB·H⁺ at m/z 77, 92, 95, 105, 118, 146, 177, and 255, respectively. The solid line is a five-point adjacent average of the data points.
Figure S11 is of the total fragmentation yield, showing the amount of recovered photofragmentation signal with respect to Laser OFF-ON parent ion signal.

**Recovered Fragmentation Yield**

\[
\text{Recovered Fragmentation Yield} = \left( \frac{\sum \text{Int}_{\text{FRAG}}}{\text{Int}_{\text{OFF}} - \text{Int}_{\text{ON}}} \right)
\]

Inspection of Figure S11 shows that for lower photon energies there are more intensity losses (likely to mass fragments below the cutoff window) than at higher energies. The noise on this plot is due to mixing of background-free gain signal (\(\text{Int}_{\text{FRAG}}\)) with the depletion signal of \(\text{Int}_{\text{OFF/ON}}\).

**Figure S11** Recovered fragmentation yield, showing the amount of recovered photofragmentation signal with respect to Laser OFF-ON parent ion signal.
Figures S12 and S13 display the UV photodepletion and photofragmentation spectra of the major AB-H⁺ photofragments m/z 135 and m/z 161, respectively. These spectra are produced upon photoexcitation of AB-H⁺ and a secondary isolation step of the major photofragment followed by photodepletion/photofragmentation of that isolated photofragment. This is done using the MSn scheme and mass-isolation feature available on the trapControl version 7.2 (Bruker Daltonics Inc.) software. It is important to note that photoexcitation of AB-H⁺ and the respective isolated photofragment, are done at the same wavelength. Therefore, the photodepletion/photofragmentation signal is dependent on the photodepletion cross-section of AB-H⁺ and the photofragmentation yield per wavelength. That is to say the spectra in Figures S12 and S13 are not fully intrinsic to those molecular fragments and may be incomplete to absorption wavelengths which the parent photofragmentation spectrum does not yield the fragment in question. However, these measurements clearly show that neither m/z 135 nor m/z 161 produce major or minor photofragments we have characterized as being from AB-H⁺.
Figure S12 The photodepletion (gas-phase absorption) spectrum of photofragment ion m/z 135 (a), along with the photofragment action spectra of its primary photofragments (b) m/z 92, (c) m/z 107, and (d) m/z 125. The solid line is a five-point adjacent average of the data points.
Figure S13 (a) The photodepletion (gas-phase absorption) spectrum of photofragment ion m/z 161. No photofragments are observed from the photodepletion of m/z 161. (Note: a low mass photofragment would not be detected).
S6 Possible heterolytic cleavage products of AB-H⁺ isomers

Due to the prevalence of Norris Type I (photo initiated α-cleavage) dissociation for neutral AB, we present Figures S14 and S15 as a guide to why products this type of dissociation would lead to for AB-H⁺. Figure S14 list all likely α-cleavage and ring elimination heterolytic products of the Ka, Kb, Ea, and Eb tautomers. Figure S15 lists these products starting with the ring-walk intermediates (shown in Scheme 4 in primary manuscript). None of the charged ions postulated in Figures S14 and S15 were seen in our photofragmentation experiment.

Figure S14 Possible heterolytic cleavage products of AB-H⁺. Products i, ii, v, and vi are identical for all isomers.
Figure S15 Possible heterolytic cleavage products of the Ea and Eb tautomers of AB-H⁺ via (4d) ring-walk intermediates.

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