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**Mapping the Intrinsic Absorption Properties and Photodegradation Pathways of the Protonated and Deprotonated Forms of the Sunscreen Oxybenzone**

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**ABSTRACT**

Sunscreens provide vital protection against the photodamaging effects of UV radiation, however, many fundamental questions remain about the detailed mechanisms by which they dissipate UV energy. One such issue is the extent to which the pH environment of an organic sunscreen molecule alters its effectiveness, both in terms of ability to absorb UV radiation, and also its potential to photodegrade. Here, we use gas-phase laser photodissociation spectroscopy for the first time to measure the intrinsic UVA-UVC absorption spectra and associated photodegradation products of protonated and deprotonated oxybenzone, away from the complications of bulk mixtures. Our results reveal that protonation state has a dramatic effect on the absorption and photodissociation properties of this sunscreen. While the UV absorption profile of oxybenzone is only modestly affected by protonation across the range from 400-216 nm, deprotonated oxybenzone displays a significantly modified absorption spectrum, with very low photoabsorption between 370-330 nm. Protonated oxybenzone primarily photofragments by rupture of the bonds on either side of the central carbonyl group, producing cationic fragments with m/z 151 and 105. Additional lower mass photofragments (e.g. m/z 95 and 77) are also observed. The production spectra for the photofragments from protonated oxybenzone fall into two distinct categories, which we discuss in the context of different excited state decay pathways. For deprotonated oxybenzone, the major photofragments observed are m/z 211 and 212, which are associated with the ejection of methane and the methyl free radical from the parent ion, respectively. Implications for the suitability of oxybenzone in its protonated and deprotonated forms as an optimum sunscreen molecule are discussed.

**1. Introduction**

In order that the skin can be protected against the photodamaging effects of UV exposure, considerable effort has been put into the development of effective sunscreens.1-4 Given the very widespread adoption of sunscreens, it is surprising that many questions remain regarding the detailed mechanisms by which they function.5-8 Over recent years, a number of advanced laser spectroscopic studies have been conducted on sunscreen molecules under highly-controlled conditions.1, 6, 9-16 These measurements can provide a detailed picture of the fundamental properties of the sunscreen molecule away from the complicated and dense environment of a real sunscreen lotion. For example, “isolated” gas-phase sunscreen molecules have been studied to provide information on the intrinsic molecular properties.14, 15, 17-19 A second group of investigations have involved highly-simplified mixtures, i.e. one sunscreen in one solvent, with transient absorption spectroscopy being applied to probe relaxation dynamics.1, 9-11, 13 Both of these distinctive approaches have been complemented by high-level quantum chemical calculations,20-25 and have provided important insights into the detailed mechanism by which a sunscreen molecule operates.

One fundamental issue that appears to have been largely ignored to date, particularly in fundamental studies, is the way in which the pH environment of the sunscreen can affect its performance,6, 26, 27 i.e. how do the properties of the protonated or deprotonated sunscreen molecule differ from those of the neutral. Recently, Li et al. showed through a series of photolysis studies performed in pure water that while neutral forms of oxybenzone do not photodecay over long timescales, the anionic form does.26 This is potentially an important issue since commercial sunscreens typically involve complex mixtures including water and alcoholic solvents. Moreover, in common usage, sunscreens are exposed to acidic and alkaline environments, with human skin and sweat being typically mildly acidic,28, 29 while chlorinated swimming pools are alkaline.30

In this work, we perform the first UV laser spectroscopy measurements on protonated and deprotonated oxybenzone, to probe the potential impact of pH on the UVA–UVC absorption profile and photodegradation products of oxybenzone (Scheme 1). Experiments are conducted on isolated, gas-phase oxybenzone ions within a novel laser-interfaced mass spectrometer. This allows us to unambiguously measure the intrinsic UV absorption profile and any associated ionic photodegradation products of the mass-selected ion,31-33 away from any complications of the bulk-phase environment.

Oxybenzone (OB) is an active ingredient that has been widely used in commercial sunscreens, and in its neutral form, is thought to be photostable even following several hours of irradiation.4, 5, 34-36 Oxybenzone was selected for study in this work as it has been the subject of several recent fundamental studies.6, 9, 10, 21, 25 Quantum chemical studies of OB have indicated that the basis of its sunscreen functionality can be traced to ultrafast decay dynamics following photoexcitation.25 Excited state intramolecular proton transfer (ESIPT) is understood to yield the keto form of OB which can undergo fast picosecond internal conversion.9 Recent transient absorption studies of OB in solution by Stavros and co-workers have produced experimental results that are consistent with these calculations, thus establishing OB as the prototype organic sunscreen for fundamental studies.9, 10

**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 laser interfaced mass spectrometry (LIMS).37, 38 This instrument has the advantages of a commercial mass spectrometer (flexible ion sources, mass selection, isolation of primary and secondary ions *via* MSn schemes, etc.), coupled with the ability to record UV photodissociation spectra in a routine manner.

OB was purchased from Alfa Aesar (Ward Hill, MA, USA) and HPLC-grade MeOH was purchased from Fisher Scientific, Inc. (Pittsburg, PA, USA), both used as received. Solutions of OB (1 × 10-4 mol dm-3) in MeOH were introduced to the mass spectrometer by ESI using typical instrumental parameters: nebulizing gas pressure of 10.0 psi, an injection rate of 0.33 mL/h, a drying gas flow rate of 8.0 L/min, and run in positive/negative ion mode at capillary temperatures of 140 oC and 100 oC to form protonated and deprotonated oxybenzone, respectively.

[OB+H]+ and [OB–H]– were 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 ~1.0 mJ across the range 400–216 nm (3.10–5.8 eV) for [OB+H]+ and ~0.3 mJ across the range 500–216 nm (2.48–5.74 eV) for [OB–H]–. Laser step sizes used for [OB+H]+ and [OB–H]– were that of 1 and 2 nm, respectively. 2 nm laser step sizes were used to record the photofragment depletion spectra of [OB+H]+ photofragments. The laser beam was focused as described in refs 37 and 38.

Photofragmentation experiments were conducted with ion accumulation times between 10–50 ms and a fragmentation time of 100 ms, thereby ensuring that each mass-selected ion packet interacted with one laser pulse to minimize the likelihood of multiphoton events. When fluorescence is neglibible,39 the UV excited gaseous ion will fragment upon excited state relaxation, yielding an action absorption spectrum by photodepletion.37, 40, 41 Photodepletion (PD) of [OB+H]+ and [OB–H]– was measured as a function of the scanned wavelength, with the photofragment production (PF) also recorded simultaneously at each wavelength:

[1]

[2]

where IntOFF and IntON are the peak intensities with laser off and on respectively; IntFRAG is the fragment intensity with the laser on; λ 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 since low masses fall outside the mass window of the ion trap. The UV photodepletion (absorption) spectra of the major OB photofragments produced upon the photoexcitation of protonated and deprotonated oxybenzone were also recorded using the MSn scheme and mass-isolation feature available on the trapControl version 7.2 (Bruker Daltonics Inc.) software.

Low-energy collision induced dissociation (CID) was employed to determine the ground state thermal fragmentation productions of [OB+H]+ and [OB-H]-. This technique was performed by applying an excitation AC voltage to the end caps of the trap to induce collisions of the trapped ions with the He buffer gas, as also described in detail previously.42, 43

Solution-phase UV absorption spectra of OB (3 × 10-5 mol dm-3) in MeOH were recorded using a UV-1800 UV-Visible spectrophotometer (Shimadzu, Kyoto, Japan) with a 10 mm UV quartz cuvette, using MeOH as the baseline solvent. The pH of each freshly-prepared OB solution was measured using a Jenway Model 3505 pH/mV/temperature meter (Cole-Palmer, Staffordshire, UK) at atmospheric pressure and room temperature. The pH meter was calibrated using NIST standard solutions buffers of pH = 7.0 and 4.0 (Fisher Scientific, Inc). To achieve a UV spectrum for [OB+H]+, solutions of OB in MeOH were acidified to a pH of 0.0 with HCl (3.0 M). Drop-wise addition of NaOH (2.0 M) to solutions of OB in MeOH enabled for the preparation of a basic solution of OB ([OB–H]–), with a final pH = 13.0, to ensure the OB was fully deprotonated (pKa 9.65).26

Calculations were performed using density functional theory at the ωB97XD/6-311++G\*\* level as implemented in Gaussian 09.44 All reported structures correspond to true minima as confirmed by frequency calculations.

**3. Results**

*3.1 Deprotonated Oxybenzone*

*3.1A Gas-Phase and Solution-Phase UV Absorption Spectra of Deprotonated Oxybenzone*

Figure 1a displays the photodepletion (gas-phase absorption) spectra of [OB–H]– (m/z 227) over the range 2.48–5.8 eV. The low-intensity band centered close to the VIS-UVA crossover region has been labeled **ID** (λmax = 3.0 eV) and does not fully approach zero photodepletion signal at 2.48 eV, the lowest energy scanned in this study. The UVA–UVB crossover point at 3.8 eV marks the onset of an intense broad photodepletion region which we label as containing two bands, **IID** (λmax = 4.0 eV) and **IIID** (λmax = 4.9 eV), to allow us to straightforwardly identify different spectral regions, with **D** indicating the deprotonated system. Photodepletion increases strongly into the UVC region.

Figure 1b presents the solution-phase absorption spectrum of OB obtained under basic conditions. Comparison of the Figure 1a and 1b spectra reveals that the gaseous ion spectrum is very similar to the solution-phase spectrum. In solution, the UVA band, **ID**, appears withλmax = 3.4 eV, and the UVB/UVC wavelength bands, **IID** and **IIID** with λmax = 4.3 eV and 5.1 eV, respectively. Notably, each gas-phase band blue-shifts by ~0.3 eV on going to solution.

The similarity of the [OB-H]- gaseous spectrum (Figure 1a) and the solution spectrum (Figure 1b) demonstrates unambiguously that the species giving rise to the solution-phase spectrum is the [OB-H]- moiety. In this context, it is instructive to compare the [OB-H]- solution-phase absorption spectra with that of neutral OB (Figure 1c). The neutral and deprotonated forms of OB display significantly different absorption profiles, with the deprotonated form providing absorption across a wider range of the UVA. In contrast, the deprotonated form absorbs significantly less UVB compared to the neutral, particularly in the vicinity of 320 nm (3.87 eV).

Finally, we note that computational chemistry calculations of the structures of [OB-H]- presented in Section 3.1C indicate that only single deprotonation isomers dominate the gas-phase (Figure 1a) and solution-phase spectra (Figure 1b).

*3.1B Photofragmentation of Deprotonated Oxybenzone*

We next turn to investigating the wavelength-dependent photofragments that are produced following photoabsorption of deprotonated oxybenzone between the range 2.48-5.78 eV. Figure 2 displays the difference (laser on - laser off) photofragment mass spectra of [OB–H]– irradiated at the maxima of bands **ID**, **IID**, and **IIID** (3.0, 4.0, and 4.9 eV, respectively). The dominant photofragments are 212 (loss of m/z 15) [3a] and m/z 211 (loss of m/z 16 from parent ion) [3b], with photofragments being produced with relatively low intensity compared to the parent ion depletion. This indicates that the major photodissociation channel across the spectral range studied is electron loss [3c]:

[OB–H]– + hʋ → ∙CH3 + m/z 212 [3a]

→ CH4 + m/z 211 [3b]

→ ∙[OB–H] + e– [3c]

Both the m/z 184 and 183 ions are also observed as minor photofragments. These correspond to the loss of 28 Da from m/z 212 and 211, respectively, and are therefore assigned as secondary fragment ions produced by the loss of CO from hot m/z 212 and 211. We note that collision-induced dissociation of [OB–H]– in the quadrupole ion trap of our instrument also produces m/z 211 and 212 as the dominant fragment ions. The loss of m/z 16 from [OB–H]– was confirmed as being associated with ejection of CH4 (and not an oxygen atom) from the parent ion by performing exact mass analysis by time of flight mass spectrometry. Whether CH4 is ejected by a concerted release or by stepwise ejection of ∙CH3 + ∙H cannot be determined in our photodissociation experiment, but the fact that m/z 211 is produced by CID as well as photoexcitation strongly suggests that CH4 is being lost in a single step. Unimolecular thermal decomposition studies of methoxybenzene have been conducted previously and have shown that methoxybenzene dissociates into methyl and phenoxy radicals,45-47 consistent with production of the m/z 212 fragment for [OB–H]– observed here. The phenoxy radical is also known to lose CO under secondary dissociation to produce the cyclopentadienyl radical, again in line with the fragmentation patterns observed here. Table 1 lists the [OB–H]– photofragment ions, along with tentative structural assignments. It is notable that all fragmentation routes result in the production of free radicals, some being diradical in nature.

Photofragment action spectra are acquired simultaneously with the photodepletion spectrum in our instrument, providing a complete picture of the wavelength-dependent fragmentation products. Figures 3b and 3c display the action spectra of the dominant m/z 211 and 212 photofragments of [OB–H]–, with the parent [OB–H]– photodepletion spectrum presented in Figure 3a for ease of comparison. The action spectrum of the m/z 211 fragment (Figure 3b) shows a broad band centered around 3.0 eV, with two lower-intensity peaks in fragment production visible at ~4.7 and ~5.4 eV. The m/z 212 fragment (Figure 3c) is produced at a lower intensity than the m/z 211 fragment, with peaks in fragment ion production at 2.6 and 4.5 eV. In contrast to m/z 211, the m/z 212 fragment intensity falls away rapidly above 4.8 eV, probably due to dissociation of m/z 212 into a secondary fragment ion. The same pattern is also evident across the lower energy band **ID** region, with m/z 211 fragment production continuing to energies above those at which the m/z 212 fragment is produced. Overall, the production profiles of m/z 211 and 212 are enhanced through bands **ID** and **IIID**, while photofragment ion production in region of band **IID** is very low.

To obtain an approximate spectrum for the electron detachment profile [3c], it is possible to subtract the photofragment intensities from the photodepletion signal. This spectrum is included in Section S1 of the Supplementary Information and reveals that at the lowest-energy scanned (2.48 eV) the electron detachment cross-section is ~50% of the photodepletion signal, while at energies corresponding to band **IID** and above, electron detachment represents ~100% of the photodepletion intensity.

*3.1C Quantum Chemical Calculations of Deprotonated Oxybenzone*

DFT geometry optimization established two forms of neutral OB, from which a search for geometric minima of the deprotonated species was initiated, with protons being removed from the hydroxyl, methoxyl, or benzoyl positions. [OB-H]- was allowed to freely rotate during optimization. Four relatively low-energy isomers (within 30 kJ mol-1 of the minimum for the gaseous structures) were identified and are shown in Scheme 2. The structures are labelled numerically in order of increasing relative energy. Table 2 displays the relative energies, with further structures being included in Section S2 of the Supplementary Information.

The [OB–H]– structures can be classed into two groups associated with the deprotonated oxygen O16 either remaining adjacent to the C7O3 carbonyl group (**D3** and **D4**), or rotating by ~180 degrees so that the deprotonated oxygen is adjacent to the benzene ring (**D1** and **D2)**. In the gas-phase, isomers **D1** and **D2** are significantly lower in energy than **D3** and **D4**, but in methanol solution, the relative energy ordering of **D2** and **D3** switch, and isomers **D2**, **D3,** and **D4** become significantly lower in relative energy. A Boltzmann distribution calculation at T = 400 K predicts that **D1** accounts for 93% of an equilibrated gaseous mixture, and 64% in solution. Under the ESI conditions used here (protic solvent), we anticipate that the ion ESI populations will be overwhelmingly **D1**.31, 32, 38 This is important as it means that the gaseous photodepletion and solution-phase absorption spectra discussed above could be assigned to just a single isomer, which considerably simplifies the analysis of the spectra presented. .31, 32, 38

The vertical electron detachment energy (VDE) was calculated for all [OB–H]– structures, including those shown in Section S2 the Supplementary Information, with values of ~2.95 eV being obtained for all of the low-energy conformers. This value agrees well with that of the isolated phenoxide moiety which has a VDE of 2.25 eV.48, 49 From the calculated VDE, it is likely that any absorbance in the UVA–UVC range for gaseous [OB–H]– will result in some electron detachment, in line with the strong propensity for electron detachment discussed in Section 3.1B.

*3.2 Protonated Oxybenzone*

*3.2A Gas-Phase and Solution-Phase UV Absorption Spectra of Protonated Oxybenzone*

Figure 4a presents the [OB+H]+ photodepletion spectra, which displays three distinct bands, labeled **IP**-**IIIP**, with λmax values at 3.50, 4.27, and 5.17 eV, respectively (**P** denotes the protonated system). Bands **IP** and **IIP** are of similar intensity and are centered within the UVA and UVB spectral regions, respectively. Band **IP** is a dominant feature of the photodepletion spectrum having a FWHM of 0.68 eV which accounts for broad absorption across the entire UVA region and into the higher-energy UVB. Band **IIP** is slightly more intense than **IP**, but narrower with a FWHM of 0.4 eV. Band **IIIP** is the least intense feature of the [OB+H]+ photodepletion spectrum, with a FWHM similar to that of band **IIP**. Bands **IIP** and **IIIP** are separated by a deep spectral valley (270-230 nm), with very low photodepletion over this UVC region.

Comparison of the measured gaseous photodepletion (absorption) spectrum of [OB+H]+ to the solution-phase absorption spectrum (Figure 4b) obtained under acidic conditions (pH 0), illustrates that the spectra agree well over both the UVA and UVB regions. In solution, bands **IP** and **IIP** peak at λmax = 3.78 and 4.29 eV, with band **IP** being blue-shifted on going from the gas-phase to solution, while the position of band **IIp**is relatively insensitive to solvation. The solution-phase spectrum obtained under near-neutral conditions (pH 7.06±0.018) is displayed in Figure 4c and displays a very similar profile across the UVA and UVB regions to the acidic spectrum. This indicates that the absorption properties of solvated OB is only modestly affected by low pH, with the sunscreen still being able to act as a strong and broad UVA and UVB absorber upon protonation. (We note that the solution-phase absorption spectrum shown here matches the previously published spectra.50)

Finally, we note that computational chemistry calculations of the structures of [OB+H]+ presented in Section 3.1C indicate that only single protonation isomers dominate the gas-phase (Figure 4a) and solution-phase spectra (Figure 4b).”

*3.2B Photofragmentation of Protonated Oxybenzone*

The difference (laser on−laser off) photofragment mass spectra of [OB+H]+ obtained following photoexcitation at the maxima of bands **IP**, **IIP**, and **IIIP** at 3.50, 4.27, and 5.17 eV, respectively, are shown in Figure 5. Photofragmentation is extensive, with the major photofragments at each energy being m/z 151 and 105 [4a] and [4b]. The m/z 95, and 77 fragments occur with significant intensity at all three excitation wavelengths, along with a number of lower intensity photofragments.

[OB+H]+ + hʋ → C6H6 + m/z 151 [4a]

→ C7H8O2 + m/z 105 [4b]

We note that low-energy CID of [OB+H]+ also results in production of the m/z 151 and 105 ions as the dominant fragments, with the m/z 95 and m/z 77 ions being produced as very minor fragments at higher collision energies. Table 3 presents assignments of all the [OB+H]+ fragment ions and highlights that the major fragments are produced through dissociation on either side of the central carbonyl group. Our structural assignment of m/z 151 and 105 match previously reported CID results of [OB+H]+.51 The m/z 77 and m/z 95 ions are common organic cations in mass spectrometry, corresponding to the benzyl cation and its complex with a water molecule.52-54

To further investigate the photofragmentation of [OB+H]+, we turn to considering the photofragment production spectra across the region from 3.0–5.8 eV. Two distinctive spectral profiles are observed for the various photofragment ions, with the m/z 151 and 105 photofragments displaying identical spectral profiles (illustrated in Figure 6b for m/z 151), and m/z 77, 95, 108 and 139 also displaying an identical profile (illustrated in Figure 6c for m/z 77). The photodepletion spectrum for [OB+H]+ is reproduced in Figure 6a, for ease of comparison. Notably, the m/z 151 photofragment is produced much more strongly through band **IIP** than band **IP**, whereas this trend is reversed for the m/z 77 photofragment spectrum. Overall, all of the photofragments are produced across the photodepletion region studied here, with very low photofragmentation or photodepletion in the “hole” region centered at 260 nm (4.77 eV). However, the relative intensities of the different photofragments change significantly across the spectral range. The complete set of photofragmentation action spectra are provided in Section S4 of the Supplementary Information.

To further investigate the relationship between the m/z 151/105 photofragments and the m/z 77/95 photofragments, we performed a series of experiments where each of the dominant m/z 151 and 105 photofragments were isolated in the ion trap, and subjected to laser excitation. This allowed us to acquire their photodepletion spectra, as well as identify their primary photofragments. Figure 7 presents the results obtained for the m/z 151 ion. This ion displays a very broad absorption between 340-260 nm (3.65-4.77 eV), with further absorption towards the high-energy region. The most intense photofragments observed from m/z 151 are m/z 123, 95, 80 and 52. Figure 8 displays the corresponding data for the m/z 105 ion, which can be seen to display one absorption band between 340-280 nm and a second, stronger band, from 270-230 nm. The main photofragments produced across these two bands are m/z 95 and 77. For both m/z 151 and 105, it is evident that m/z 95 and 77 can therefore be produced as secondary photofragments at energies above 300 nm. However, for both m/z 151 and m/z 105, absorption is negligible across the key band **IP** region, i.e. at wavelengths longer than 340 nm. This leads us to conclude that the m/z 77, 95, 108 and 139 primary photofragments from [OB+H]+ are being produced in this VIS-UVA region through a different pathway (evident in the distinctive production spectrum) from the m/z 151 and 105 photofragments.

*3.2C Further Discussion of the Photodissociation Dynamics of Protonated Oxybenzone*

While a detailed mapping of the photodissociation dynamics of [OB+H]+ will require time-resolved measurements of the production of the various photofragments, some initial insight can be gained from considering whether excited state decay is statistical or non-statistical. In general, excited state decay can be classified as statistical when the observed photofragments match those obtained when the ground electronic state is subjected to thermal dissociation, as in CID. Non-statistical (or non-ergodic) processes occur when dissociation proceeds directly from the excited state without significant involvement of a conical intersection to bring the system back to the ground electronic state in the vicinity of the starting geometry.55 For non-statistical decay, the photofragments will differ significantly in relative intensity and identity from those observed under thermal fragmentation conditions.

Our measurements on [OB+H]+ have revealed that the photofragments produced in the region of band **ID** display relative intensities that are significantly different from those observed upon CID, i.e. the intensities of the m/z 139, 108, 95, and 77 ions are considerably more intense than in CID, suggesting that the excited state surface accessed in this region is not simply evolving through a conical intersection back to the ground state in the region of the vertical transition. A non-statistical pathway appears to be dominant in this region, with direct dissociation from the excited state. Such a situation is highly undesirable for a sunscreen molecule, and merits further investigation in dynamical studies in condensed-phase media.

*3.2D Quantum Chemical Calculations of Protonated Oxybenzone*

[OB+H]+ isomers were identified by attaching a proton to each oxygen atom on neutral OB prior to optimization, and allowing the ion to rotate freely during optimization. Four relatively low-energy isomers (within 30 kJ mol-1 of the minimum for the gaseous structures) were identified (Scheme 2), with the relative energies being displayed in Table 2. Comprehensive structures are included in Section S2 of the Supplementary Information.

The lowest energy [OB+H]+ isomers are closer in relative energy than those of [OB–H]–, as well as in average nuclear displacement. The lowest energy **P1** and **P2** structures, which are only distinguished by a methyl group rotation, and are close enough in energy that their combined Boltzmann population accounts for more than 90% of the gaseous population (66% and 31% respectively). This trend is carried over in methanol conditions where **P1** accounts for 41% and **P2** for 55% of the average population. We anticipate that the ESI ion ensemble will be dominated by a mixture of **P1** and **P2** in our experiment (protic spray solvent).31, 32, 38 (These rotamers are expected to produce identical photodepletion spectra at the resolution of our spectrometer.56) It is important that our calculations reveal the presence of effectively just a single isomer, as it means that the gaseous photodepletion and solution-phase absorption spectra discussed above could be assigned to just a single isomer, simplifying the analysis of the spectra compared to similar systems where distinctive multiple protonation isomers are present .31, 32, 38

**4. Concluding Remarks**

The photodepletion spectra of [OB-H]- and [OB+H]+ obtained in this work clearly illustrate the effect that protonation state can have on the absorption properties of a typical organic sunscreen molecule. While the effect of protonation is relatively modest (primarily associated with shifting of the UVA region absorption), deprotonation has a more significant effect, with photoabsorption being significantly decreased between 370-330 nm compared to the neutral system. Our comparison of the solution-phase and gas-phase spectra indicates that these differences occur both in solution and in the gas-phase, so will be important even within the complex environment of a sunscreen mixture.

One of the novel aspects of our gas-phase experiment is that it allows us to obtain a full picture of the photofragments produced following excitation. [OB-H]- and [OB+H]+ photodissociate by very distinct pathways, with [OB-H]- primarily fragmenting via pathways associated with loss of the anisole methyl group, while [OB+H]+ dissociates by rupture of the molecule on either side of the central carbonyl group. For [OB-H]-, the fragmentation pathway appears to follow those of neutral anisoles and negatively charged flavinoids,57 which are known to eject methyl radicals and hydrogen atoms. For [OB+H]+, the dissociation pathways branch from the central protonated carbonyl, in line with the known mass spectrometric fragmentation behavior of such ions.58

For [OB-H]-, it is important to note that it produces large quantities of electrons following photoexcitation, as well as generating free radicals by all of its dissociation routes. This is a highly undesirable property for a sunscreen molecule, which leads to the question of how this behavior will be modified on going to the condensed phase. It is well established that the propensity of an anionic molecule to photodetach will be quenched upon solvation,59 so that the photofragmentation pathways are likely to become relatively more important in condensed media. Recent work by Li et al. has found that oxybenzone photodegrades in aqueous alkaline solutions made from pure water.26 The authors were broadly concerned with indirect photodegradation of oxybenzone in surface and salt waters (due to environmental and wastewater management implications) by transient photosensitizers such as the triplet excited states of dissolved organic matter (3DOM), hydroxy radicals (∙OH), and singlet oxygen (1O2). Their experiments confirmed the presence of free ∙OH in their photolytic systems as well and the ability for ∙OH and 3DOM to photodegrade oxybenzone. The gas-phase work conducted here is in line with these observations and provides further information on the details on the active photodegradation pathways.

In considering how well the protonated and deprotonated forms of OB behave as sunscreen molecules, it is also important to consider the ability of the ionic forms of the molecule to undergo ultrafast excited state decay back to the electronic ground state from where excess energy can be dissipated as heat energy. This process is now well understood for neutral oxybenzone, following detailed quantum chemical calculations by Domcke and co-workers, who found that excited state decay involves proton transfer from the enol to keto forms, followed by rapid internal conversion.25 Our calculations predict that the keto-enol site of oxybenzone is the protonation/deprotonation location, so it would be unsurprising to discover that the neutral ultrafast decay mechanism is significantly perturbed in the presence of acid or base. In [OB+H]+, we have found evidence for two distinctive decay pathways in the UVA region, which is notable since it is well documented that locally excited states (such as a UVA π-π\* transition) can couple with nearby charge-transfer states.60-62 Interestingly, Dean et al. have demonstrated that this situation occurs for sinapoyl malate,15 a photoprotection molecule found in plants. Future time-resolved measurements are warranted to more fully investigate this.

In conclusion, we report the first gas-phase laser photodissociation of the protonated and deprotonated forms of the model sunscreen, oxybenzone. The results presented provide important new insights into how protonation behavior can affect the intrinsic properties of an organic sunscreen and demonstrate the utility of laser-interfaced mass spectrometry for mapping the photodegradation pathways of such systems.

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**Conflicts of Interest**

There are no conflicts to declare.

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**TABLE 1.** Proposed structures for the low-intensity ionic fragments of [OB-H]- (m/z 227) produced during CID and laser photoexcitation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Fragment Mass (m/z)** | **Proposed Structure of Fragment** | **m/z lost from [OB–H]–** | **Fragment Results from Loss of Neutral** | **Observed in CID a** | **Observed in Laser Photoexcitation a** |
| 212 |  | 15 | ·CH3 | * (s) | * (m) |
| 211 |  | 16 | CH4  (or ∙CH3 + ∙H) | * (s) | * (w) |
| 184 |  | 43 | ∙CH3 + CO |  | * (vw) |
| 183 |  | 44 | CH4 + CO  (or ∙CH3 + ∙H + CO) |  | * (vw) |

a s (strong), m (medium), w (weak), and vw (very weak).

**TABLE 2.** Calculated relative energies and physical properties of oxybenzone dependent on pH. Calculated at the ωB97XD/6-311++G\*\* level.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Structure** | **Relative Energy (kJ mol-1) a, b** | **VDE (eV) c** |
| **[OB-H]-** | **D1** | 0.0 (0.0) | 3.00 |
| **D2** | 8.2 (5.1) | 3.00 |
| **D3** | 21.0 (3.8) | 2.89 |
| **D4** | 29.8 (8.7) | 2.87 |
| **[OB+H]+** | **P1** | 0.0 (1.0) |  |
| **P2** | 1.8 (0.0) |  |
| **P3** | 9.9 (9.8) |  |
| **P4** | 16.6 (12.7) |  |

a Relative electronic energies are zero-point energy corrected. b Values in parentheses are calculated in methanol. c VDE = E(neutral at optimized anion geometry) – E(anion).

**TABLE 3**. Proposed structures for the low-intensity ionic fragments of [OB+H]+ (m/z 229) produced during CID and laser photoexcitation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Fragment Mass (m/z)** | **Proposed Structure of Fragment** | **m/z lost from [OB+H]+** | **Fragment Results from Loss of Neutral** | **Observed in CID a** | **Observed in Laser Photoexcitation a** |
| 151 |  | 78 |  | * (vs) | * (vs) |
| 139 |  | 90 | - |  | * (w) |
| 108 |  | 121 | - |  | * (vw) |
| 105 |  | 124 |  | * (m) | * (s) |
| 95 b |  | - | - | * (vw) | * (m) |
| 77 |  | 152 |  | * (vw) | * (m) |

a vs (very strong), s (strong), m (medium), w (weak), and vw (very weak). b m/z 95 likely m/z 77 + 18.

**SHEMES AND FIGURES**

**SCHEME 1.** Schematic diagram of oxybenzone (OB) with atom labels.

**SCHEME 2.** Low energy isomers of [OB-H]- and [OB+H]+ obtained at the ωB97XD/6-311++G\*\* level.

**FIGURE CAPTIONS**

**FIGURE 1.** **(a)** Gas-phase photodepletion spectrum of deprotonated oxybenzone ([OB–H]–). The solid line is a five-point adjacent average of the data points. **(b)** Solution-phase absorption spectrum of OB at pH = 13.0. **(c)** Solution-phase absorption spectrum of OB at pH = 7.06.

**FIGURE 2.** Photofragment difference (laser on−laser off) mass spectrum of [OB–H]–, excited at three **(a-c)** photodepletion maxima (Bands **ID**, **IID**, and **IIID**) of **(a)** 3.0, **(b)** 4.0, and **(c)** 4.9 eV. \*represents the depleted parent ion signal at m/z 227.

**FIGURE 3. (a)** Gas-phase UV absorption (photodepletion) spectra of [OB–H]–. **(b-c)** Photofragment production spectrum of two major photofragments at m/z 211 and m/z 212, respectively. The solid line is a five-point adjacent average of the data points.

**FIGURE 4. (a)** Gas-phase photodepletion spectrum of protonated oxybenzone ([OB+H]+). The solid line is a five-point adjacent average of the data points. **(b)** Solution-phase absorption spectra of OB at pH = 0.0. **(c)** Solution-phase absorption spectra of OB at pH = 7.06.2.

**FIGURE 5.** Photofragment difference (laser on−laser off) mass spectrum of [OB+H]+, excited at the photodepletion maxima (Bands **IP**, **IIP**, and **IIIP**) of **(a)** 3.50, **(b)** 4.27, and **(c)** 5.17 eV. \*represents the depleted parent ion signal at m/z 229.

**FIGURE 6. (a)** Gas-phase UV absorption (photodepletion) spectra of [OB+H]+. **(b-c)**Photofragment production spectra of the photofragments at m/z 151 and m/z 77, respectively. The solid line is a five-point adjacent average of the data points.

**FIGURE 7.** The photodepletion spectrum (absorption) of photofragment ion m/z 151 (a), along with the photofragment action spectra of its primary photofragments (b) m/z 52, (c) m/z 80, (d) m/z 95, and (e) m/z 123. The solid line is a five-point adjacent average of the data points.

**FIGURE 8.** The photodepletion spectrum (absorption) of photofragment ion m/z 105 (a), along with the photofragment action spectra of its primary photofragments (b) m/z 77 and (c) m/z 95. The solid line is a five-point adjacent average of the data points.

Scheme 1



Scheme 2



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8



Graphical Abstract

Supplementary Information

**Mapping the Intrinsic Absorption Properties and Photodegradation Pathways of the Protonated and Deprotonated Forms of the Sunscreen Oxybenzone**

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**Supplementary Material**

S1. Electron Detachment Spectrum of [OB–H]–

S2. Geometries of Deprotonated and Protonated Oxybenzone and Selected Physical Properties

S3. Collision-Induced Dissociation of Deprotonated and Protonated Oxybenzone

S4. Additional Photofragment Action Spectra for Protonated Oxybenzone

**S1. Electron Detachment Spectrum of [OB**–**H]**–

Relative electron detachment was determined according to the following equation:

[1]

The remaining percent of raw photodepletion signal (IntON–IntOFF) once the contribution of all photofragments are removed is the electron detachment intensity. IntFRAG is the signal intensity for a unique m/z fragment where all are summed to account for a total (> 50 m/z) photofragment intensity.



**Figure S1.** Relative electron detachment intensity of photodissociation of [OB–H]–.

**S2. Extensive Geometries of Deprotonated and Protonated Oxybenzone and Selected Physical Properties**

Only the lowest energy structures were listed within the manuscript. Here are all inspected structures which include high energy deprotonation site and protomer species. Table S1 includes the energies relative to the lowest energy deprotonated (**D**) or protonated (**P**) structure. Scheme S1 shows the structures found in Table S1.

**Table S1.** Calculated relative energies and physical properties of OB dependent on pH. Calculated at the wB97XD/6-311++G\*\* level.

|  |  |  |  |
| --- | --- | --- | --- |
| **Structure** | **Relative Energy (kJ mol-1) a,b** | **VDE (eV) c** | **Vertical Dipole Moment (D)** |
| **D1** | 0.0 (0.0) | 3.00 | 4.2 |
| **D2** | 8.2 (5.1) | 3.00 | 4.7 |
| **D3** | 21.0 (3.8) | 2.89 | 6.0 |
| **D4** | 29.8 (8.7) | 2.87 | 7.9 |
| **D5** | 159 (150) | 2.45 | 3.4 |
| **D6** | 175 (181) | 2.21 | 5.2 |
| **D7** | 175 (179) | 2.17 | 2.5 |
| **D8** | 191 (158) | 2.25 | 5.9 |
| **D9** | 191 (198) | 1.75 | 5.2 |
| **D10** | 210 (201) | 1.94 | 2.9 |
| **P1** | 0.0 (1.0) |  |  |
| **P2** | 1.8 (0.0) |  |  |
| **P3** | 9.9 (9.8) |  |  |
| **P4** | 16.6 (12.7) |  |  |
| **P5** | 139 (92) |  |  |

**Scheme S1.** All the structures from Table S1. Arrows indicate the deprotonation site for all **D** structures.



**S3. Collision-Induced Dissociation of Deprotonated and Protonated Oxybenzone**

Low-energy collision-induced dissociation (CID) was performed on isolated deprotonated and protonated OB to determine the thermal fragments. Figures S2 and S3 present the relative intensities of the deprotonated and protonated OB parent ion respectively, and the corresponding fragment ions as a function of applied CID energy.



**Figure S2.** CID fragmentation decay curve for deprotonated OB (m/z 227) upon low energy CID. Onset plots for production of the associated fragment ions (m/z 212 and m/z 211) are also shown. The curved lines included with the data points are a three-point adjacent average of such data points and are provided as a viewing guide, to emphasize the profile for an individual fragment.



**Figure S3.** CID fragmentation decay curve for protonated OB (m/z 229) upon low energy CID. Onset plots for production of the associated fragment ions **(a)** m/z 151 and 105, and **(b)** m/z 95 and 77 are also shown. The curved lines included with the data points are a three-point adjacent average of such data points and are provided as a viewing guide, to emphasize the profile for an individual fragment.

**S4. Additional Photofragment Action Spectra for Protonated Oxybenzone**



**Figure S4.** Protonated OB photofragmentation action spectra of **(a)** m/z 105 and **(b)** m/z 151. The solid line is a five-point adjacent average of the data points.



**Figure S5.** Protonated OB photofragmentation action spectra of **(a)**m/z 77, **(b)** m/z 95, **(c)** m/z 108, and **(d)** m/z 139. The solid line is a five-point adjacent average of the data points.