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Supplementary Information

1 Sodium Cationization Can Disrupt the Intramolecular Hydrogen Bond that Mediates the

- 2 Sunscreen Activity of Oxybenzone
- 3 Jacob A. Berenbeim,^a Natalie G. K. Wong,^a Martin C. R. Cockett,^a Giel Berden,^b Jos
- 4 Oomens,^b Anouk M. Rijs,^b and Caroline E. H. Dessent^{a†}

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- 6 ^aDepartment of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.
- 7 ^bRadboud University, Institute for Molecules and Materials, FELIX Laboratory,
- 8 Toernooiveld 7, Nijmegen, The Netherlands
- 9 [†] Corresponding author: E-mail caroline.dessent@york.ac.uk

- 11 S1 Isomer schematic for bare OB
- 12 S2 Laser power dependence on UV photodepletion
- 13 S3 IR mode analysis for M⁺•OB (M⁺=Na⁺, K⁺, Rb⁺)
- 14 S4 $\pi \rightarrow \pi^*$ NTOs for M⁺•OB (M⁺=Na⁺, K⁺, Rb⁺)
- 15 S5 Similarity combination for select M⁺•OB (M⁺=Na⁺, K⁺, Rb⁺)

16 S1 Isomer Schematic for Bare OB

17 Within the manuscript we refer to oxybenzone (OB) isomers as either I, II, or III. Scheme S1

- 18 outlines these structures. Attempts to find a keto OB structure with the intramolecular
- 19 hydrogen bond all converged to isomer I, however, a minima was found for a non-hydrogen
- 20 bonded keto structure which was 115 kJ/mol higher in energy than isomer I. Due to this
- 21 exceptional high energy difference the non-hydrogen bonded keto isomer was not considered
- 22 in this study.



- 24 Scheme S1 Bare oxybenzone isomers with the intramolecular hydrogen bond (I: top), twisted (II:
- 25 middle), and non-hydrogen bonded (III: bottom).

26 S2 Laser power dependence on UV photodepletion

Laser power measurements were conducted on Na⁺•OB and Rb⁺•OB at 288 nm and 360 nm, 27 respectively, to test for the presence of multiphoton effects. These wavelengths correspond 28 closely to each ions λ max as determined by UV photodepletion. No power measurement of 29 K⁺•OB was collected under the assumption that its behaviour would be within the limits 30 defines by Na⁺ and Rb⁺ experiments. Figures S1-2 show the photodepletion intensities 31 (Int_{OFF}-Int_{ON}) at laser pulse energies 0.6-1.5 mJ. The Y-axis has been plotted as a natural log 32 scale and data fit to a power function of the form $Y = A X^{k}$, where A is a scalar accounting 33 for signal intensity and k is the slope (proportional to the number of absorbed photons). K 34 values fit to less than 1 for both the Na⁺ and Rb⁺ ion species. This result indicates that 35 photodepletion here is not multiphoton in nature. That k < 1 likely indicates saturation of the 36

- 37 linear transition and that a lower laser power could have been used to increase the intensity
- 38 resolution in this region. For this reason a laser energy of 0.3 mJ was used for K⁺•OB.





40 Figure S1 Power dependent measurements for Na⁺•OB photodepletion near λmax (288 nm).



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42 Figure S2 Power dependent measurements for $Rb^+ OB$ photodepletion near λmax (360 nm).

44 S3 IR mode analysis for M⁺•OB (M⁺= Na⁺, K⁺, Rb⁺)

- 45 We present descriptive vector analysis for isomers matching the IRMPD results. The modes
- 46 presented are highly mixed with ring motions (and due to complexity these carbon ring
- 47 modes are not described).



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49 Figure S3 Major IR modes of (d) Na⁺•OB. Calculated at the B3LYP/cc-pVTZ level.



52 Figure S4 Major IR modes of (a) K⁺•OBd. Calculated at the B3LYP/cc-pVTZ level.



54 Figure S5 Major IR modes of (a) Rb⁺•OB. Calculated at the B3LYP/cc-pVTZ level.

55 S4 π π^* NTOs for M⁺•OB (M⁺= Na⁺, K⁺, Rb⁺)

- 57 **Table S1** TD-DFT transition strengths and natural transition orbitals for initial $\pi\pi^*$ states of
- 58 M⁺•OB (M=Na⁺, K⁺, and Rb⁺) ions, and bare OB calculated at the M06-2X/cc-pVTZ level of
- 59 theory

Complex	π π*	Osc.	Occupied	Unoccupied
Na ⁺ •OB (d)	S2	0.5	Silve.	- 200 -
	85	0.1		
K⁺•OB	S2	0.4		
(d)			- *** * * *	1997 - C. J.
	S5	0.1		
K⁺•OB	S1	0.2	·	
(a)			H. St.	- 3 5 000
	S3	0.4	jan ja	
Rb⁺•OB	S1	0.2		
(a)			AT St.	3.5 000
	S3	0.4	A MA	1000 A
OB	S2	0.2	2	
(I)			17. T	4 5 0 0 3.

Supplementary Information

S3 0.3



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62 S5 Similarity combination for select M⁺•OB (M⁺=Na⁺, K⁺, Rb⁺)

63 The fit between the experimental IRMPD spectra and spectra generated by DFT calculations

64 was assessed by comparing the cosine similarity of the lowest-energy structures. Fit

65 similarity is assessed as the cosine of the angle θ between two spectral vectors A and B,

66 which is calculated as the dot product of these vectors divided by the product of their

67 Euclidian norms, according to:

similarity =
$$\cos \theta = \frac{A \cdot B}{\|A\| \|B\|} = \frac{\sum_{i=1}^{N} A_i B_i}{\sqrt{\sum_{i=1}^{N} A_i^2} \sqrt{\sum_{i=1}^{N} B_i^2}}$$

68 [1]

69 The most analogous spectral vectors will have the smallest angle between them and a

70 similarity value that approaches unity. Here within the SI we utilize a transformation of the

71 spectral vector as proposed by Kempkes et al. to reduce the intensity mismatches and

72 prioritize frequency overlap.¹ The issue of variability of IRMPD spectral intensities is

73 discussed in Polfer's review² article and in further detail by Berden et al.³ The amplitude

74 modification transformation is:

$$A_{i}^{transform} = \log\left(\frac{A_{i}}{A_{max}} + c\right)$$

$$[2]$$

76 Where c is constant for all spectral vectors of which modification will adjust the contributions

of low amplitude bands and, similarly, experimental noise. We have used a value of 10^{-8} for c

78 here as suggested by the Kempkes et al.

79 Table S2 presents the spectral matching score with the amplitude modification next to the

80 unmodified similarity value in parenthesis. The values in Table S2 are rounded to 2

significant figures, lending the match for Na⁺ (**d**) motif to be one but in reality it is not a

82 perfect (unity) match. Inspection of Figure S6 shows that three or more significant figures are

83 necessary when comparing amplitude modified values.

84 Figure S6 shows the combination similarity scores for isomer mixtures of (a:c) and (a:d) of

85 K⁺•OB. While the IR spectrum of isomer (c) alone did show a similarity to the experimental

86 results, the combination of isomers (a:d) scored a more identical match to those results than

87 did (a:c), across a variety of mixture ratios.

- 88 **Table S2** The spectral matching score based on cosine similarity are given for the various
- 89 coordination motif spectra of M⁺•OB (M⁺= Na⁺, K⁺, Rb⁺) calculated at the B3LYP/cc-pVTZ
- 90 level of theory compared to IRMPD. Values in parenthesis are similarities without the
- 91 amplitude modification.

	Matching Score				
Motif	Na ⁺ •OB	K⁺•OB	Rb ⁺ •OB		
a	0.930 (0.529)	0.943 (0.852)	0.967 (0.835)		
b	0.977 (0.727)	0.868 (0.709)	0.924 (0.775)		
с	0.959 (0.667)	0.895 (0.812)	0.946 (0.781)		
d	1.001 (0.952)	0.802 (0.812)	0.929 (0.777)		
e	0.960 (0.649)	0.820 (0.824)	0.871 (0.433)		
a:c ^a	-	0.947 (0.876)	-		
a:d ^b	-	0.955 (0.938)	-		

92 ^{a,b} For mixture ratios, see corresponding maxima plotted in Figure S6



93

94 Figure S6 Similarity matches for combinations of K⁺•OB isomers (a:c) (in black) and isomers (a:d)
95 (in blue) with and without the amplitude modification as noted by the y-axis.

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