Supplement of

Enhanced photodegradation of dimethoxybenzene isomers in/on ice compared to in aqueous solution

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Supplemental Section S1. Details of light absorption modeling

Justification for a single machine learning model for all three DMOB isomers. As shown in Supplemental Figure S26 and Supplemental Table S5, the machine learning (ML) model achieves a training $R^2$ of 0.981 and a testing $R^2$ of 0.965, along with a training mean absolute error (MAE) of 1.42 nm and a testing MAE of 1.88 nm. Since a universal ML model is fitted to predict the vertical excitation wavelengths ($\lambda$) for all three DMOB isomers, we broke down the overall MAE to assess the ML model performance for each molecule. As shown in Supplemental Table S5, the negligible variations in the MAE implies that our model can generate predictions with no bias towards a particular molecule. This trend justified our approach to predict excitation wavelengths for all three molecules using only one ML model. Meanwhile, the overall training and testing MAE for DMOB isomers, as well as the average testing MAE for molecules in solution (1.93 ± 0.16 nm) and at the air-ice interface (1.82 ± 0.23 nm), suggest that this model can be generalized to predict excitation wavelengths for all three isomers in both solution and at the air-ice interface.
Additional information for hyperparameters used to compute Bispectrum Component (BC). Before describing the atomic environment for the three DMOB isomers using a bispectrum component, a set of hyperparameters must be carefully defined. First, the cut-off radius for hydrogen, carbon and oxygen ($R_{cut,H}$, $R_{cut,C}$ & $R_{cut,O}$) are set to 1.5, 2.5, and 3 Å respectively, which corresponds to approximately second-neighbor distances. Meanwhile, to reflect the relative importance for the chemical environment with respect to each atom type, the dimensionless weight factors ($\omega_H$, $\omega_C$ & $\omega_O$) of 1.0, 2.0, and 3.0 are set accordingly. Lastly, to ensure a sufficiently large initial feature space for the LASSO model development, a $2j_{max}$ parameter is chosen to be 14, which results in a total of 858 bispectrum components.

Formulation of linear decomposition analysis. To pinpoint the relative importance to the predictions of $\lambda$ with respect to functional groups of DMOB isomers, a linear decomposition analysis can be performed and formulated as:

$$
\lambda_{predicted} = \lambda_0 + \lambda_{predicted,OCH_3} + \lambda_{predicted,C_6H_4}
$$

$$
\lambda_{Decomposed} = \frac{(\lambda_{predicted,OCH_3} + \lambda_{predicted,C_6H_4})}{\lambda_{predicted} - \lambda_0}
$$

In the above equation, $\lambda_0$ is the intercept of the LASSO model; $\lambda_{predicted,OCH_3}$ and $\lambda_{predicted,C_6H_4}$ represent predictions contributions from the methoxy groups and from the phenyl ring; and $\lambda_{Decomposed}$ is defined to express the decomposition with respect to the functional groups by percentage.

Supplemental Section S2. Detailed description of sample preparation methods

We placed samples in 10-ml glass beakers (Pyrex, inside diameter 22 mm) and covered them with nylon film (McMaster-Carr, approximately 25 µm thick, secured in place with an o-ring) to reduce evaporation and contamination while allowing sample illumination. As discussed in our previous work with guaiacol (Hullar et al. 2020), we prepared samples using one of five different methods: 1) in an aqueous solution, where we dissolved the test compound in MQ water to give a final concentration of 1.0 µM, then we placed 10 ml of solution in a beaker and covered. 2) Freezer frozen solution, prepared identically to aqueous solution with 10 ml of a 1.0 µM aqueous solution placed in a 10 ml beaker, covered, then placed in a laboratory freezer (-20 °C) for at least 3 hours. 3) Liquid nitrogen frozen solution, which we prepared identically to aqueous solution, then placed it in a pan filled to a depth of 2 cm with liquid nitrogen; sample freezing took approximately 90 seconds. 4) Vapor deposition of gas-phase test compound to the surface of ice. Following an approach previously described (Hullar et al. 2020, Hullar et al. 2018), first we placed 10 ml of MQ water in a beaker, covered it with film, and froze it in a laboratory freezer at -20 ºC. We removed and uncovered the frozen samples, and directed a nitrogen stream containing gas-phase dimethoxybenzene at the ice surface for 15 or 30 s. We then recovered the samples and placed them back in a laboratory freezer. 5) Vapor deposited to nature-identical snow, which was produced as described in our previous work (Hullar et al. 2020). We first made nature-identical snow crystals in a custom-built machine derived from previous work (Bones and Adams 2009, Nakamura 1978, Schleef et al. 2014). The snow machine operates in a cold room at -15 °C, nucleates supersaturated water vapor onto nylon wires, forming snow crystals. This snow is then collected and placed in a 500 ml HDPE bottle. To deposit dimethoxybenzene onto the snow, we passed nitrogen from a tank in the cold room first through 500 ml of laboratory-made snow (to condition the nitrogen stream with water vapor), then through a glass container holding 0.4 g of DMOB, and then through a 500-ml HDPE bottle holding the snow to be illuminated, where the DMOB is deposited. 1,2-DMOB is a liquid at room temperature but a solid at -20 °C, while 1,3-DMOB is a liquid at both temperatures and 1,4-DMOB a solid; vapor pressures at 25 °C are 0.057, 0.030, and 0.021 kPa, respectively (USEPA 2021). We then gently mixed the treated snow and transferred it to beakers, tamped it down 10 mm below the top edge of the beaker, and covered it with nylon film.
**Supplemental Table S1. Experimental light intensity correction factors.** Light intensity correction factors for the experimental illumination system, determined as the ratio of aqueous \( j_{2NB} \) in a given position divided by the corresponding value in the reference position (B2). These factors were used to normalize photodegradation rates to the photon flux in each position. Illuminated samples were put in columns B and C, while dark samples (which were uncorrected for photon flux) were placed in columns A and D.

| Row | A  | B  | C  | D  |
|-----|----|----|----|----|
| 1   | 0.18 | 1.00 | 0.80 | 0.55 |
| 2   | 0.44 | 1.00 | 0.83 | 0.89 |
| 3   | 0.61 | 1.06 | 0.99 | 1.10 |
| 4   | 0.18 | 1.08 | 0.95 | 0.77 |
**Supplemental Table S2. Light absorbance values.** Measured, predicted, and modeled light absorbance values for a) 1,2-, b) 1,3-, and c) 1,4-DMOB. Molar absorption coefficients (columns 2 and 4) were measured for aqueous and predicted for the air-ice interface. Modeled absorbance values (columns 5 and 6) were computed using molecular modeling techniques. See footnotes and text for details.

*a) 1,2-Dimethoxybenzene*

Modeled parameters used to predict air-ice interface spectrum:
- Peak wavelength shift from aqueous to air-ice interface: 2.4 nm
- Peak height ratio, air-ice interface / aqueous: 1.17
- Peak width ratio, air-ice interface / aqueous: 0.94

| Wavelength (nm) | Molar absorption coefficient (M^{-1} cm^{-1}) | Modeled absorbance (AU) |
|-----------------|-----------------------------------------------|-------------------------|
|                 | Aqueous (measured)^a | Aqueous (measured) standard error ^a | Air-ice interface (predicted)^b | Aqueous | Air-ice interface |
| 250             | 519               | 0.84                      | 0                         | 0       | 0                   |
| 251             | 572               | 0.80                      | 0                         | 0       | 0                   |
| 252             | 631               | 1.34                      | 0                         | 0       | 0                   |
| 253             | 707               | 0.68                      | 0                         | 0       | 0                   |
| 254             | 795               | 1.01                      | 613                       | 0       | 0                   |
| 255             | 897               | 1.21                      | 682                       | 0       | 0                   |
| 256             | 1010              | 0.85                      | 857                       | 0       | 0                   |
| 257             | 1132              | 0.79                      | 975                       | 0       | 0                   |
| 258             | 1272              | 1.18                      | 1113                      | 0       | 0                   |
| 259             | 1422              | 0.85                      | 857                       | 0       | 0                   |
| 260             | 1585              | 0.74                      | 1250                      | 0       | 0                   |
| 261             | 1760              | 1.23                      | 1424                      | 0       | 0                   |
| 262             | 1950              | 0.81                      | 1610                      | 0       | 0                   |
| 263             | 2153              | 1.62                      | 1794                      | 0       | 0                   |
| 264             | 2349              | 1.81                      | 2019                      | 0       | 0                   |
| 265             | 2571              | 8.27                      | 2258                      | 0.003   | 0                   |
| 266             | 2745              | 9.05                      | 2497                      | 0.008   | 0                   |
| 267             | 2909              | 13.44                     | 2749                      | 0.017   | 0.001               |
| 268             | 3070              | 13.07                     | 3033                      | 0.031   | 0.005               |
| 269             | 3236              | 16.57                     | 3233                      | 0.059   | 0.016               |
| 270             | 3383              | 8.75                      | 3445                      | 0.091   | 0.037               |
| 271             | 3490              | 13.07                     | 3657                      | 0.150   | 0.077               |
| 272             | 3564              | 11.46                     | 3843                      | 0.236   | 0.112               |
| 273             | 3610              | 20.29                     | 4019                      | 0.367   | 0.155               |
| 274             | 3594              | 9.20                      | 4134                      | 0.556   | 0.263               |
| 275             | 3498              | 15.85                     | 4219                      | 0.755   | 0.439               |
| 276             | 3337              | 19.54                     | 4227                      | 1.022   | 0.632               |
| 277             | 3196              | 14.64                     | 4133                      | 1.375   | 0.813               |
| 278             | 3109              | 16.90                     | 3958                      | 1.662   | 1.026               |
| 279             | 3043              | 7.75                      | 3772                      | 1.859   | 1.276               |
| 280             | 2883              | 7.66                      | 3641                      | 2.050   | 1.552               |
|    |       |     |      |      |      |
|----|-------|-----|------|------|------|
| 281| 2486  | 3.20| 3566 | 2.096| 1.886|
| 282| 1960  | 3.23| 3373 | 2.008| 2.137|
| 283| 1415  | 3.33| 2846 | 1.995| 2.273|
| 284| 978   | 2.34| 2229 | 1.994| 2.386|
| 285| 649   | 1.26| 1549 | 1.843| 2.452|
| 286| 434   | 0.81| 1014 | 1.612| 2.422|
| 287| 284   | 0.45| 677  | 1.410| 2.260|
| 288| 186   | 0.62| 426  | 1.240| 2.014|
| 289| 117   | 0.39| 271  | 1.035| 1.753|
| 290| 75    | 0.97| 174  | 0.823| 1.459|
| 291| 47    | 1.00| 105  | 0.623| 1.167|
| 292| 30    | 0.31| 63   | 0.439| 0.937|
| 293| 19    | 0.79| 40   | 0.301| 0.717|
| 294| 12    | 1.29| 24   | 0.211| 0.477|
| 295| 8.17  | 0.51| 15   | 0.147| 0.296|
| 296| 5.35  | 0.55| 10   | 0.098| 0.202|
| 297| 3.40  | 0.47| 6.26 | 0.072| 0.156|
| 298| 2.15  | 0.80| 3.81 | 0.065| 0.116|
| 299| 1.37  | 0.86| 2.42 | 0.056| 0.072|
| 300| 0.87  | 0.97| 1.47 | 0.040| 0.046|
| 301| 0.55  | 0.47| 0.89 | 0.028| 0.031|
| 302| 0.35  | 0.73| 0.57 | 0.022| 0.016|
| 303| 0.22  | 0.58| 0.34 | 0.017| 0.005|
| 304| 0.14  | 0.93| 0.21 | 0.011| 0.001|
| 305| 0.089 | 0.37| 0.13 | 0.005| 0   |
| 306| 0.057 | 0.99| 0.080| 0.002| 0   |
| 307| 0.036 | 0.93| 0.048| 0.000| 0   |
| 308| 0.023 | 0.67| 0.031| 0.001| 0   |
| 309| 0.014 | 0.30| 0.019| 0.004| 0   |
| 310| 0.0092 |0.87 | 0.011| 0.005| 0   |
| 311| 0.0058 |0.40 | 0.0072| 0.003| 0   |
| 312| 0.0037 |0.44 | 0.0043| 0.001| 0   |
| 313| 0.0023 |0.67 | 0.0026| 0   | 0   |
| 314| 0.0015 |0.75 | 0.0017| 0   | 0   |
| 315| 0.00094|0.69 | 0.0010| 0   | 0   |
| 316| 0.00060|0.44 | 0.00062| 0   | 0   |
b) 1,3-Dimethoxybenzene
Modeled parameters used to predict air-ice interface spectrum:

- Peak wavelength shift from aqueous to air-ice interface: 5.2 nm
- Peak height ratio, air-ice interface / aqueous: 0.91
- Peak width ratio, air-ice interface / aqueous: 1.27

| Wavelength (nm) | Molar absorption coefficient (M$^{-1}$ cm$^{-1}$) | Modeled absorbance (AU)$^c$ |
|-----------------|-----------------------------------------------|----------------------------|
|                 | Aqueous (measured)$^a$ | Aqueous (measured) standard error $^a$ | Air-ice interface (predicted)$^b$ | Aqueous | Air-ice interface |
| 250             | 536  | 2.20 | 522 | 0 | 0 |
| 251             | 600  | 2.25 | 571 | 0 | 0 |
| 252             | 670  | 2.72 | 626 | 0 | 0 |
| 253             | 758  | 2.34 | 690 | 0 | 0 |
| 254             | 853  | 2.00 | 758 | 0 | 0 |
| 255             | 967  | 2.70 | 836 | 0 | 0 |
| 256             | 1098 | 2.25 | 925 | 0 | 0 |
| 257             | 1235 | 2.61 | 1023| 0 | 0 |
| 258             | 1395 | 2.99 | 1111| 0 | 0 |
| 259             | 1558 | 3.04 | 1225| 0 | 0 |
| 260             | 1745 | 2.67 | 1343| 0 | 0 |
| 261             | 1938 | 2.52 | 1464| 0 | 0.001 |
| 262             | 2158 | 3.41 | 1606| 0.002| 0.004 |
| 263             | 2393 | 3.15 | 1747| 0.008| 0.005 |
| 264             | 2570 | 43.20| 1903| 0.012| 0.004 |
| 265             | 2796 | 32.11| 2070| 0.027| 0.006 |
| 266             | 2984 | 33.64| 2215| 0.066| 0.015 |
| 267             | 3165 | 39.48| 2339| 0.122| 0.024 |
| 268             | 3322 | 35.93| 2504| 0.160| 0.040 |
| 269             | 3494 | 33.04| 2646| 0.226| 0.084 |
| 270             | 3663 | 39.52| 2780| 0.356| 0.127 |
| 271             | 3859 | 41.74| 2914| 0.510| 0.139 |
| 272             | 3997 | 45.15| 3023| 0.624| 0.192 |
| 273             | 4010 | 45.44| 3148| 0.789| 0.288 |
| 274             | 3889 | 43.95| 3272| 1.035| 0.422 |
| 275             | 3638 | 47.63| 3407| 1.258| 0.579 |
| 276             | 3443 | 35.54| 3526| 1.423| 0.725 |
| 277             | 3385 | 32.08| 3627| 1.582| 0.843 |
| 278             | 3476 | 35.40| 3653| 1.683| 0.986 |
| 279             | 3479 | 30.13| 3607| 1.742| 1.179 |
| 280             | 3190 | 40.92| 3470| 1.718| 1.315 |
| 281             | 2592 | 44.15| 3290| 1.592| 1.422 |
| 282             | 1867 | 2.10 | 3149| 1.513| 1.505 |
| 283             | 1260 | 2.44 | 3091| 1.464| 1.551 |
| 284             | 844  | 2.76 | 3112| 1.318| 1.570 |
| 285             | 541  | 2.36 | 3178| 1.109| 1.586 |
| 286             | 348  | 1.82 | 3166| 0.903| 1.590 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 287 | 224 | 2.14 | 2976 | 0.741 | 1.545 |
| 288 | 142 | 2.15 | 2603 | 0.595 | 1.439 |
| 289 | 89  | 1.90 | 2076 | 0.454 | 1.276 |
| 290 | 56  | 1.75 | 1584 | 0.347 | 1.140 |
| 291 | 36  | 1.88 | 1147 | 0.254 | 1.020 |
| 292 | 22  | 1.77 | 839  | 0.183 | 0.884 |
| 293 | 13  | 1.91 | 586  | 0.130 | 0.755 |
| 294 | 8.3 | 1.17 | 433  | 0.095 | 0.648 |
| 295 | 5.3 | 1.62 | 304  | 0.067 | 0.545 |
| 296 | 2.9 | 1.74 | 213  | 0.040 | 0.432 |
| 297 | 1.8 | 1.54 | 150  | 0.023 | 0.346 |
| 298 | 1.2 | 1.26 | 104  | 0.016 | 0.280 |
| 299 | 0.72| 1.89 | 71   | 0.015 | 0.223 |
| 300 | 0.45| 1.79 | 49   | 0.012 | 0.189 |
| 301 | 0.28| 1.50 | 34   | 0.007 | 0.159 |
| 302 | 0.18| 2.08 | 23   | 0.003 | 0.122 |
| 303 | 0.11| 1.79 | 16   | 0.001 | 0.087 |
| 304 | 0.069| 2.01| 11   | 0     | 0.061 |
| 305 | 0.043| 1.98| 7.5  | 0     | 0.044 |
| 306 | 0.027| 2.04| 5.2  | 0     | 0.036 |
| 307 | 0.017| 1.13| 3.4  | 0     | 0.029 |
| 308 | 0.011| 1.64| 2.2  | 0     | 0.021 |
| 309 | 0.0067| 0.98| 1.5  | 0     | 0.016 |
| 310 | 0.0042| 1.41| 1.0  | 0     | 0.013 |
| 311 | 0.0026| 1.87| 0.73 | 0     | 0.010 |
| 312 | 0.0016| 1.92| 0.52 | 0     | 0.006 |
| 313 | 0.0010| 0.97| 0.36 | 0     | 0.003 |
| 314 | 0.00064| 1.72| 0.25 | 0     | 0.002 |
| 315 | 0.00040| 0.81| 0.17 | 0     | 0.002 |
| 316 | 0   | 0.12 | 0    | 0     | 0.001 |
| 317 | 0   | 0.080| 0    | 0     | 0     |
| 318 | 0   | 0.055| 0    | 0     | 0     |
| 319 | 0   | 0.038| 0    | 0     | 0     |
| 320 | 0   | 0.026| 0    | 0     | 0     |
| 321 | 0   | 0.019| 0    | 0     | 0     |
| 322 | 0   | 0.013| 0    | 0     | 0     |
| 323 | 0   | 0.0089| 0   | 0     | 0     |
| 324 | 0   | 0.0061| 0   | 0     | 0     |
| 325 | 0   | 0.0042| 0   | 0     | 0     |
| 326 | 0   | 0.0029| 0   | 0     | 0     |
| 327 | 0   | 0.0020| 0   | 0     | 0     |
| 328 | 0   | 0.0014| 0   | 0     | 0     |
| 329 | 0   | 0.00093| 0   | 0     | 0     |
| 330 | 0   | 0.00068| 0   | 0     | 0     |
| 331 | 0   | 0.00046| 0   | 0     | 0     |
| 332 | 0   | 0.00015| 0   | 0     | 0     |
c) 1,4-Dimethoxybenzene
Modeled parameters used to predict air-ice interface spectrum:
  Peak wavelength shift from aqueous to air-ice interface: 1.6 nm
  Peak height ratio, air-ice interface / aqueous: 1.06
  Peak width ratio, air-ice interface / aqueous: 0.92

| Wavelength (nm) | Molar absorption coefficient (M⁻¹ cm⁻¹) | Modeled absorbance (AU)⁶ |
|-----------------|----------------------------------------|---------------------------|
|                 | Aqueous (measured)¹ | Aqueous (measured)¹ | Air-ice interface (predicted)¹ |
|                 | standard error ¹ | | |
| 250             | 167 | 1.08 | 0 | 0 | 0 |
| 251             | 163 | 0.80 | 0 | 0 | 0 |
| 252             | 165 | 0.78 | 0 | 0 | 0 |
| 253             | 171 | 0.90 | 0 | 0 | 0 |
| 254             | 181 | 1.24 | 0 | 0 | 0 |
| 255             | 197 | 0.81 | 176 | 0 | 0 |
| 256             | 216 | 1.14 | 174 | 0 | 0 |
| 257             | 238 | 1.13 | 178 | 0 | 0 |
| 258             | 267 | 1.07 | 187 | 0 | 0 |
| 259             | 298 | 0.64 | 201 | 0 | 0 |
| 260             | 336 | 1.36 | 222 | 0 | 0 |
| 261             | 379 | 1.43 | 247 | 0 | 0 |
| 262             | 428 | 1.15 | 280 | 0 | 0 |
| 263             | 482 | 1.34 | 316 | 0 | 0 |
| 264             | 540 | 2.01 | 361 | 0 | 0 |
| 265             | 603 | 2.33 | 411 | 0 | 0 |
| 266             | 667 | 2.78 | 471 | 0 | 0 |
| 267             | 739 | 2.63 | 536 | 0 | 0 |
| 268             | 819 | 3.53 | 602 | 0 | 0 |
| 269             | 895 | 2.57 | 681 | 0 | 0 |
| 270             | 975 | 3.04 | 760 | 0 | 0 |
| 271             | 1060 | 3.76 | 843 | 0 | 0 |
| 272             | 1149 | 4.06 | 933 | 0 | 0 |
| 273             | 1244 | 4.71 | 1025 | 0 | 0 |
| 274             | 1341 | 4.73 | 1124 | 0 | 0 |
| 275             | 1446 | 4.90 | 1227 | 0 | 0 |
| 276             | 1552 | 5.16 | 1338 | 0 | 0 |
| 277             | 1655 | 5.55 | 1456 | 0 | 0 |
| 278             | 1755 | 6.39 | 1581 | 0 | 0 |
| 279             | 1851 | 5.56 | 1696 | 0 | 0 |
| 280             | 1947 | 6.34 | 1820 | 0.002 | 0 |
| 281             | 2026 | 6.66 | 1932 | 0.002 | 0 |
| 282             | 2119 | 7.15 | 2044 | 0.001 | 0 |
| 283             | 2192 | 6.64 | 2131 | 0.000 | 0 |
| 284             | 2251 | 7.24 | 2236 | 0.002 | 0 |
| 285             | 2302 | 8.09 | 2324 | 0.006 | 0 |
| 286             | 2321 | 7.13 | 2393 | 0.009 | 0 |
| 287             | 2326 | 7.94 | 2441 | 0.016 | 0 |
|   |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|
| 288 | 2314  | 7.61  | 2469  | 0.024 |       |
| 289 | 2276  | 6.80  | 2466  | 0.036 |       |
| 290 | 2221  | 7.56  | 2434  | 0.053 | 0.002 |
| 291 | 2150  | 6.80  | 2380  | 0.081 | 0.008 |
| 292 | 2072  | 7.00  | 2305  | 0.114 | 0.014 |
| 293 | 1983  | 6.56  | 2214  | 0.137 | 0.018 |
| 294 | 1875  | 5.49  | 2110  | 0.181 | 0.028 |
| 295 | 1761  | 5.73  | 2000  | 0.275 | 0.066 |
| 296 | 1633  | 5.77  | 1867  | 0.379 | 0.132 |
| 297 | 1472  | 4.95  | 1714  | 0.475 | 0.211 |
| 298 | 1301  | 4.19  |        |       |       |
| 299 | 1114  | 3.89  |        |       |       |
| 300 | 917   | 3.03  |        |       |       |
| 301 | 727   | 2.42  |        |       |       |
| 302 | 554   | 2.16  |        |       |       |
| 303 | 415   | 1.50  |        |       |       |
| 304 | 303   | 1.08  |        |       |       |
| 305 | 221   | 0.83  |        |       |       |
| 306 | 157   | 1.03  |        |       |       |
| 307 | 109   | 0.16  |        |       |       |
| 308 | 74    | 0.98  |        |       |       |
| 309 | 52    | 0.49  |        |       |       |
| 310 | 35    | 0.88  |        |       |       |
| 311 | 25    | 0.58  |        |       |       |
| 312 | 17    | 0.71  |        |       |       |
| 313 | 13    | 0.57  |        |       |       |
| 314 | 8.8   | 0.49  |        |       |       |
| 315 | 6.1   | 0.40  |        |       |       |
| 316 | 4.2   | 0.61  |        |       |       |
| 317 | 2.9   | 0.25  |        |       |       |
| 318 | 2.0   | 0.62  |        |       |       |
| 319 | 1.4   | 0.35  |        |       |       |
| 320 | 1.0   | 1.23  |        |       |       |
| 321 | 0.67  | 1.13  |        |       |       |
| 322 | 0.47  | 0.94  |        |       |       |
| 323 | 0.32  | 1.44  |        |       |       |
| 324 | 0.22  | 0.85  |        |       |       |
| 325 | 0.16  | 0.90  |        |       |       |
| 326 | 0.11  | 0.97  |        |       |       |
| 327 | 0.075 | 0.51  |        |       |       |
| 328 | 0.052 | 0.78  |        |       |       |
| 329 | 0.036 | 0.29  |        |       |       |
| 330 | 0.025 | 0.52  |        |       |       |
| 331 | 0.017 | 0.98  |        |       |       |
| 332 | 0.012 | 0.62  |        |       |       |
| 333 | 0.0083| 1.14  |        |       |       |
| 334 | 0.0057| 0.53  |        |       |       |
| 335 | 0.0040| 0.64  |        |       |       |
| DMOB | Absorbance | E1%1cm | SE of slope | SE of slope | SE of slope | SE of slope |
|------|------------|--------|-------------|-------------|-------------|-------------|
| 336  | 0.0028     | 0.77   | 0.0011      | 0           | 0           | 0           |
| 337  | 0.0019     | 0.14   | 0.00073     | 0           | 0           | 0           |
| 338  | 0.0013     | 0.49   | 0.00049     | 0           | 0           | 0           |
| 339  | 0.00092    | 0.96   | 0           | 0           | 0           | 0           |
| 340  | 0.00064    | 0.53   | 0           | 0           | 0           | 0           |
| 341  | 0.00044    | 0.47   | 0           | 0           | 0           | 0           |

For each DMOB, we measured absorbance spectra in five aqueous solutions (10-1000 µM) at 25 °C using a UV-2501PC spectrophotometer (Shimadzu) in 1.0 cm cuvettes against a MQ reference cell. For each wavelength, we calculated the base-10 molar absorption coefficient as the slope of the linear regression of measured absorbance versus the DMOB concentration. Standard errors are the SE of the slope of the regression line. At wavelengths from 296-316, 296-315, and 313-341 nm for 1,2-, 1,3-, and 1,4-DMOB respectively, the calculated molar absorption coefficients were <5 M⁻¹ cm⁻¹ and very noisy. To better estimate molar absorption coefficients in these ranges, we used the measured data from 290-296, 290-296, and 307-313 nm for each compound respectively, plotted λ vs ln(εDMOB,λ), then used the slope of the linear regression to determine εDMOB,λ at wavelengths longer than these ranges.

| Predicted molar absorption coefficients at the air-ice interface, based on aqueous absorbance values adjusted using modeled absorbance changes between solution and the air-ice interface. See text for details. |
| Results of computationally-determined absorbance spectra in aqueous solution and at the air-ice interface in arbitrary absorbance units. See text for details. |
Supplemental Table S3. Illumination experiment measured parameters. Summary of parameters determined from illumination experiments, summarized for each DMOB isomer and experimental condition. “avg” represents the mean value for each isomer and sample treatment, “SD” is the standard deviation, and “95% CI” is the 95 percent confidence interval of the mean.

|           | \( n^a \) | \( j_{\text{DMOB}} \) (min\(^{-1}\))\(^b \) | \( k'_{\text{DMOB, dark}} \) (min\(^{-1}\))\(^c \) | \( j_{\text{DMOB,exp}} \) (min\(^{-1}\))\(^d \) | \( j^*_{\text{DMOB}} \) (min\(^{-1}/s\)^{-1})\(^e \) | \( j_{\text{2NB}} \) (s\(^{-1}\))\(^f \) |
|-----------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
|           | avg      | SD              | 95% CI          | avg      | SD              | 95% CI          | avg      | SD              | 95% CI          |
| 1,2-DMOB  |          |                 |                 |          |                 |                 |          |                 |                 |
| Aqueous   | 3        | 9.3E-06         | 4.7E-06         | 1.2E-05  | 3.5E-06         | 2.2E-06         | 5.5E-06  | 3.1E-06         | 7.8E-06         | 1.9E-03         | 1.1E-03         | 2.7E-03         | 3.2E-03         | 2.7E-04         | 6.6E-04         |
| Freezer frozen solution | 3 | -4.8E-06 | 2.9E-05 | 7.1E-05 | -4.9E-05 | 1.6E-05 | 3.9E-05 | -4.8E-06 | 2.9E-05 | 7.1E-05 | -1.5E-03 | 9.9E-03 | 2.5E-02 | 2.9E-03 | 1.8E-04 | 4.5E-04 |
| Liquid nitrogen frozen solution | 4 | 5.0E-06 | 7.8E-06 | 1.2E-05 | -1.1E-06 | 2.8E-06 | 4.4E-06 | 4.5E-06 | 7.9E-06 | 1.3E-05 | 1.9E-03 | 3.4E-03 | 5.4E-03 | 2.6E-03 | 1.9E-04 | 3.0E-04 |
| Vapor-deposited to ice surface | 3 | 1.8E-04 | 1.7E-04 | 4.2E-04 | 2.1E-05 | 2.3E-05 | 5.7E-05 | 1.5E-04 | 1.6E-04 | 4.0E-04 | 2.9E-02 | 2.2E-02 | 5.5E-02 | 5.2E-03 | 2.6E-03 | 6.5E-03 |
| Vapor-deposited to snow | 5 | 4.3E-05 | 1.5E-05 | 1.9E-05 | -2.1E-06 | 2.8E-05 | 3.5E-05 | 3.3E-05 | 9.9E-06 | 1.2E-05 | 2.7E-02 | 8.4E-03 | 1.0E-02 | 1.2E-03 | 3.1E-05 | 3.9E-05 |
| 1,3-DMOB  |          |                 |                 |          |                 |                 |          |                 |                 |
| Aqueous   | 6        | 1.1E-05         | 1.0E-05         | 1.1E-05  | 1.5E-05         | 1.4E-05         | 1.5E-05  | -3.4E-06 | 9.1E-06 | 9.5E-06 | -1.1E-03 | 2.9E-03 | 3.0E-03 | 3.3E-03 | 2.1E-04 | 2.2E-04 |
| Freezer frozen solution | 0 |          |                 |          |                 |                 |          |                 |                 |
| Liquid nitrogen frozen solution | 3 | 2.8E-05 | 7.9E-06 | 2.0E-05 | -1.1E-07 | 2.3E-06 | 5.7E-06 | 2.8E-05 | 9.0E-06 | 2.2E-05 | 1.3E-02 | 4.2E-03 | 1.1E-02 | 2.1E-03 | 3.8E-05 | 9.6E-05 |
| Vapor-deposited to ice surface | 0 |          |                 |          |                 |                 |          |                 |                 |
| Vapor-deposited to snow | 5 | 2.2E-04 | 5.1E-05 | 6.3E-05 | 1.6E-04 | 3.7E-05 | 4.6E-05 | 6.2E-05 | 4.9E-05 | 6.1E-05 | 5.4E-02 | 4.5E-02 | 5.6E-02 | 1.2E-03 | 7.4E-05 | 9.2E-05 |
| 1,4-DMOB  |          |                 |                 |          |                 |                 |          |                 |                 |
| Aqueous   | 3        | 2.0E-05         | 6.3E-06         | 1.6E-05  | 7.1E-06         | 6.0E-06         | 1.5E-05  | 1.3E-05         | 2.7E-06         | 6.7E-06         | 4.3E-03         | 7.3E-04         | 1.8E-03         | 3.1E-03         | 1.2E-04         | 3.0E-04         |
| Freezer frozen solution | 0 |          |                 |          |                 |                 |          |                 |                 |
| Liquid nitrogen frozen solution | 3 | 4.5E-05 | 3.4E-06 | 8.5E-06 | -2.3E-07 | 8.2E-06 | 2.0E-05 | 4.3E-05 | 6.2E-06 | 1.5E-05 | 1.5E-02 | 3.6E-03 | 9.0E-03 | 3.0E-03 | 5.2E-04 | 1.3E-03 |
| Vapor-deposited to ice surface | 1 | 1.1E-04 | 7.1E-05 | 8.8E-05 | 5.5E-05 | 4.7E-05 | 5.9E-05 | 5.2E-05 | 9.5E-05 | 1.2E-04 | 1.4E-02 | 2.5E-02 | 3.1E-02 | 4.2E-03 | 5.6E-04 | 6.9E-04 |
| Vapor-deposited to snow | 8 | 4.2E-04 | 2.7E-04 | 2.2E-04 | 2.2E-04 | 2.4E-04 | 2.0E-04 | 2.0E-04 | 1.7E-04 | 1.4E-04 | 1.1E-01 | 9.1E-02 | 7.6E-02 | 1.6E-03 | 6.9E-04 | 5.8E-04 |

\( a \) Number of experiments  
\( b \) The pseudo-first-order rate constant for DMOB loss during sample illumination, obtained as the slope of ln([DMOB]/[DMOB]$_0$) vs t, where [DMOB]$_0$ was corrected for variations in light flux at each illumination position  
\( c \) Rate constant for DMOB loss in dark controls  
\( d \) Dark-corrected experimental photodegradation rate constant, obtained by subtracting \( k'_{\text{DMOB, dark}} \) from \( j_{\text{DMOB}} \)  
\( e \) Photon flux-normalized photodegradation rate constant, normalized by dividing the dark-corrected experimental photodegradation rate constant (\( j_{\text{DMOB,exp}} \)) by the daily measured \( j_{\text{2NB}} \) value  
\( f \) Daily measured 2NB photolysis rate constant, measured using the same sample preparation method as the DMOB sample, except in the case of snow samples. For snow samples, \( j_{\text{2NB}} \) was measured in aqueous solution and multiplied by previously determined correction factor of 0.38 to to give a snow \( j_{\text{2NB}} \) value.
Supplementary Table S4. Rate constants for light absorption. Integrated rate constants for light absorption, determined for each DMOB isomer by multiplying the measured (aqueous) or predicted (air-ice interface) molar absorption coefficient by the experimental or Summit conditions photon flux, then summing the resulting values. Ratios for each isomer are the air-ice interface rate constant divided by the aqueous rate constant.

| Compound | Experimental light conditions | | | Summit light conditions |
|----------|-----------------------------|---|---|-----------------------------|
|          | Rate constant for light absorption | Rate constant ratio | | Rate constant for light absorption | Rate constant ratio |
|          | (photons molecule\(^{-1}\) s\(^{-1}\)) | | | (photons molecule\(^{-1}\) s\(^{-1}\)) | |
|          | Aqueous | Air-ice interface | aqueous | Aqueous | Air-ice interface | aqueous |
| 1,2-DMOB | 6.8E-06 | 1.2E-05 | 1.7 | 3.4E-08 | 5.1E-08 | 1.5 |
| 1,3-DMOB | 6.5E-06 | 3.4E-05 | 5.3 | 1.7E-08 | 2.8E-06 | 170 |
| 1,4-DMOB | 1.0E-04 | 1.2E-04 | 1.1 | 8.1E-05 | 8.3E-05 | 1.0 |

\(\text{a Calculated using } \Sigma (2303/N_A I_\lambda \varepsilon_\lambda), \text{ where } 2303 \text{ is a factor for units and base conversion (1000 cm}^3 \text{ L}^{-1}), N_A \text{ is Avogadro’s number (6.022 x 1023 molecules mol}^{-1}), I_\lambda \text{ is the experimental or modeled photon flux at each wavelength (photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}), \text{ and } \varepsilon_\lambda \text{ is the wavelength-dependent molar absorptivity for each DMOB (M}^{-1} \text{ cm}^{-1}).\)

Supplemental Table S55. Machine learning training and testing errors. Summary of training and testing Mean Absolute Error (MAE) for each DMOB molecule in the machine learning model of light absorption. Both the training and the testing MAE are computed by averaging the MAE from the 5-fold cross validation scheme.

|          | Training MAE (nm) | | | Testing MAE (nm) | |
|----------|-------------------|---|---|-------------------|---|
| 1,2-DMOB | 1.38              | | | 1.84              | |
| 1,3-DMOB | 1.39              | | | 1.92              | |
| 1,4-DMOB | 1.50              | | | 1.87              | |
| Average & Std | 1.42 ± 0.056 | | | 1.88 ± 0.031 | |
Supplemental Figures S1a-S12h. Results for individual illumination experiments. Results for individual illumination experiments showing dimethoxybenzene concentration changes over time for illuminated samples (filled diamonds, solid regression line) and dark controls (open diamonds, dashed regression line). Date for each experiment is given in yyyymmdd format. Compounds are color-coded purple (1,2-DMOB), maroon (1,3-DMOB), and green (1,4-DMOB). Sample type is given in the upper right corner of each graph. Each data point represents an individual sample beaker, with two illuminated samples and one dark control sample per time point. Initial DMOB concentration, measured as average measured aqueous concentration in the two time zero illuminated samples, is given in the chart title. Wherever possible, for each compound the same Y axis scale was used for related sample treatments to allow easier comparison. Average data for each experiment type are summarized in Table S3.
Supplemental Figure S13. Experimental and modeled photon fluxes. Experimental and TUV-modeled photon fluxes from 300-400 nm (panel a) and 270-310 nm (panel b). TUV-modeled flux is for Summit, Greenland at noon on the summer solstice (see text for details of modeling parameters). a) Summit actinic flux is given at 0.1 nm resolution from 300-350 nm, then 1 nm resolution from 350-400 nm; experimental flux was determined at 1 nm and interpolated to 0.1 nm resolution presented here. b) TUV and experimental fluxes at 0.1 nm resolution.
Supplemental Figure S14. Light absorbance spectra for DMOB isomers. Measured and modeled spectra for 1,2-, 1,3-, and 1,4-DMOB. For each isomer, solid black lines are the measured absorbance spectra in aqueous solution; solid and dashed colored lines are the aqueous and air-ice interface spectra estimated using molecular modeling (right axis); dashed black lines show the air-ice interface absorbance values predicted by combining
the measured aqueous absorbance spectra with the modeling results (see text for details). Modeled absorbance values (right axis) are arbitrary and not intended to correspond to actual molar absorption coefficients.

Supplemental Figure S15. Linear decomposition analysis for DMOB isomers. Linear Decomposition Analysis for the $\lambda_{\text{predictions}}$ for the three DMOB isomers. Bars and values represent the contributions of the phenyl ring ($C_6H_4$) and methoxy group ($OCH_3$) to the predicted excitation wavelength ($\lambda_{\text{decomposed}}$) for 1,2- (top), 1,3- (middle) and 1,4-DMOB (bottom) in solution (blue) and at the air-ice interface (cyan).
Supplemental Figure S16. Action spectra for DMOB light absorbance. Action spectra for light absorbance, determined for each DMOB isomer by multiplying the aqueous (solid lines) or predicted air-ice interface (dashed lines) molar absorption coefficient by the experimental or Summit conditions photon flux at each wavelength. Results are given at 1 nm resolution. The value at a given wavelength was determined as

$$\frac{2303}{N_A} I_\lambda \varepsilon_\lambda$$

where 2303 is a factor for units and base conversion (1000 cm$^3$ L$^{-1}$), $N_A$ is Avogadro’s number (6.022 × 10$^{23}$ molecules mol$^{-1}$), $I_\lambda$ is the photon flux at each wavelength (photons cm$^{-2}$ s$^{-1}$), and $\varepsilon_\lambda$ is the wavelength-dependent molar absorption coefficient for each DMOB (M$^{-1}$ cm$^{-1}$). The area under each curve is the overall rate constant for light absorbance; these are tabulated in Table S4. For 1,2- and 1,3-DMOB, the Summit conditions rate constants have been scaled for readability.
Supplemental Figure S17. Photodegradation rate constant ratios for shifted absorbance curves. Predicted changes in photodegradation rate constants ($j^*_{DMOB}$) for 1,2- and 1,3-DMOB due to shifting of absorbance relative to the unshifted value where the peak is centered at 280 nm. Rate constants were estimated using calculated quantum yields, aqueous absorbance spectra shifted hypsochromically (towards shorter wavelengths) or bathochromically (towards longer wavelengths), and either experimental photon fluxes (solid lines) or the TUV-modeled actinic flux for midday on the summer solstice at Summit, Greenland (dashed lines). See Figure 4 for the equivalent figure for 1,2- and 1,4-DMOB.
Supplemental Figure S18. Guaiacol photodegradation rate constants for various illumination conditions. Absorbance shift impacts on calculated guaiacol photodegradation rate constants under several photon flux conditions. The black line represents rate constants calculated using TUV-modeled photon fluxes for Summit, Greenland at noon on the summer solstice; the red line uses the photon fluxes for experiments in this work; the green lines were calculated using the two experimental light conditions used in our previous guaiacol work (Hullar et al. 2020). The difference in photon fluxes between the solid red (DMOB) and green (LC2) lines is due to changing the cover material for the sample beaker: the current DMOB work uses a nylon film, while the previous LC2 guaiacol work used a polyethylene film.
Supplemental Figure S19. Absorbance spectra for DMOBs compared to assumed Gaussian peaks. Measured absorbance spectra and assumed Gaussian peaks for 1,2- and 1,4-dimethoxybenzene. Solid lines are the measured aqueous absorbance spectra, and the dashed lines are the Gaussian distributions chosen to approximate the measured spectra. The 1,2-DMOB and 1,4-DMOB surrogates have peak locations, standard deviations, and peak heights of 274 and 287 nm, 6.6 and 8.3 nm, and 368 and 2335 M$^{-1}$ cm$^{-1}$ respectively. Black dashed line (right axis) represents the TUV-modeled actinic flux for Summit, Greenland.
Supplemental Figure S20. Model compound absorbance spectra for various peak locations. Hypothetical model compound peak location with various position shifts. The solid black line represents the default center position of the assumed Gaussian peak (280 nm, standard deviation 7 nm, peak height 3000 M$^{-1}$ cm$^{-1}$), while blue and red lines show hypsochromically and bathochromically shifted peak locations, respectively. The black dashed line (right axis) represents the TUV-modeled actinic flux for Summit, Greenland.
Supplemental Figure S21. Model compound photodegradation rate constants for various peak locations. Predicted changes to photodegradation rate constants ($j_{\text{max}}$) and the corresponding lifetimes resulting from absorbance shifts for a hypothetical model compound. Rate constants ($j_{\text{max}}$) and lifetimes were calculated using an assumed quantum yield of 1, modeled actinic flux for Summit conditions, and an assumed Gaussian absorbance spectrum (peak molar absorption coefficient 3000 M$^{-1}$ cm$^{-1}$, standard deviation of 7 nm) with varying peak positions. a) Ratio of shifted to unshifted $j_{\text{max}}$ for varying hypsochromic (blue) or bathochromic (red) absorbance shifts. b) Calculated rate constants ($j_{\text{max}}$) and lifetimes at various peak positions.
Supplemental Figure S22. Model compound absorbance spectra for various peak widths. Assumed absorption spectrum for a Gaussian hypothetical model compound showing baseline peak width (black line, standard deviation 7 nm) and various other peak widths (red and blue lines). Black dashed line (right axis) represents the TUV-modeled actinic flux for Summit, Greenland.
Supplemental Figure S23. Model compound photodegradation rate constants for various peak widths.
Predicted changes to photodegradation rate constants and photochemical lifetimes resulting from variations in peak width (represented by various standard deviations of an assumed Gaussian absorbance spectrum) for a hypothetical model compound. The solid black line shows the baseline peak width (7 nm), while the red and blue lines show the rate constants and lifetimes for various peak widths and shifts.
Supplemental Figure S24. Model compound absorbance spectra for various molar absorption coefficients. Assumed absorption spectra for a Gaussian hypothetical model compound showing baseline peak height (black line, molar absorption coefficient = 3000 M⁻¹ cm⁻¹) and various other molar absorption coefficients (red and blue lines). The black dashed line (right axis) represents the TUV-modeled actinic flux for Summit conditions.
Supplemental Figure S25. Model compound photodegradation rate constant for various molar absorption coefficients. Predicted changes to photodegradation rate constants and photochemical lifetimes resulting from molar absorption coefficient changes for a hypothetical model compound. The solid black line shows the baseline peak height (molar absorption coefficients = 3000 M$^{-1}$ cm$^{-1}$), while the red and blue lines show the rate constants and lifetimes for various molar absorption coefficients and shifts.
**Supplemental Figure S26. Machine learning parity plots.** Parity plots for our unified machine learning model for the three DMB isomers. The $R^2$ and MAE are computed from the average $R^2$ and MAE from the 5-fold cross validation scheme. During each fold of the cross-validation scheme, a total of 888 frames were used in the training, 222 frames were used in the testing.

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