



Direct photolysis of  
carbonyl compounds

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# Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets

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## Abstract

Gas phase photolysis is an important tropospheric sink for many carbonyl compounds, however the significance of direct photolysis of carbonyl compounds dissolved in cloud and fog droplets is uncertain. We develop a theoretical approach to assess the importance of aqueous photolysis for a series of carbonyls that possess carboxyl and hydroxyl functional groups by comparison with rates of other atmospheric processes. We use computationally and experimentally derived Henry's law parameters, hydration equilibrium parameters, aqueous hydroxyl radical (OH) rate constants, and optical extinction coefficients to identify types of compounds that will not have competitive aqueous photolysis rates. We also present molecular dynamics simulations of atmospherically relevant carbonyl compounds designed to estimate gas and aqueous phase extinction coefficients. In addition, experiments designed to measure the photolysis rate of glyceraldehyde, an atmospherically relevant water soluble organic compound, reveal that aqueous quantum yields are highly molecule-specific and cannot be extrapolated from measurements of structurally similar compounds. We find that only three out of the 92 carbonyl compounds investigated, pyruvic acid, 3-oxobutanoic acid, and 3-oxopropanoic acid, may have aqueous photolysis rates that exceed the rate of oxidation by dissolved OH. For almost all carbonyl compounds lacking  $\alpha$ ,  $\beta$  conjugation, atmospheric removal by direct photolysis in cloud and fog droplets can be neglected.

## 1 Introduction

Oxidation of volatile organic precursors in the atmosphere produces highly functionalized water soluble compounds (Saxena and Hildemann, 1996). These oxidation products typically contain several types of functional groups including carboxyls, carbonyls, hydroxyls, and peroxides. Low volatility products will partition into the particle phase while high volatility compounds will remain in the gas phase. In the presence of clouds and fog, water-soluble gas and particle phase compounds will partition into the aque-

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ous phase (Facchini et al., 1999; Ervens et al., 2011). Compounds dissolved in atmospheric water droplets may react with dissolved oxidants or undergo direct photolysis by actinic radiation. Aqueous oxidation processes have garnered much attention among atmospheric researchers (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Vione et al., 2006), but the implications of direct aqueous photolysis remain uncertain.

It is well established that carbonyls weakly absorb radiation at wavelengths around 280 nm due to a forbidden  $\pi^* \leftarrow n$  transition. Photodissociation of carbonyls in the gas phase is well studied, with the absorption cross sections and quantum yields published for a variety of compounds (Sander et al., 2011). However, aqueous photolysis quantum yields at actinic wavelengths of carbonyls dissolved in cloud and fog droplets are not well established. In light of the limited data, we strive to determine which atmospherically relevant carbonyls may have competitive photolytic removal rates in cloud and fog droplets. In our previous publication (Epstein and Nizkorodov, 2012), we determined that compounds with large Henry's law constants ( $>10^4 \text{ Matm}^{-1}$ ) that do not suffer from significant suppression of photolysis by the solvent may have aqueous photolysis rates that are competitive with gas phase photolysis. In this manuscript, we apply this analysis to a set of atmospherically relevant carbonyl compounds with the additional constraint that aqueous photolysis rates must be competitive with aqueous oxidation by hydroxyl radical for direct aqueous photolysis to be a significant carbonyl sink.

For photolabile carbonyl compounds in the gas phase such as formaldehyde or acetone, direct photolysis is often competitive with oxidation by gas phase hydroxyl radical (OH) radicals (Epstein and Nizkorodov, 2012). Aqueous photolysis lifetimes depend on the optical extinction coefficients, actinic flux, and the photolysis quantum yields. In general, rate constants governing the aqueous photolysis of carbonyls will be lower than gas phase photolysis rate constants for several reasons: absorption cross sections of carbonyl compounds can undergo a hypsochromic shift of approximately 10 nm upon dissolution in water (Xu et al., 1993), aqueous quantum yields may be suppressed due

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to the excited state relaxation by the solvent molecules and the cage-effect (Calvert and Pitts, 1966), the fraction of the carbonyl in the photolabile (non-hydrated) form may be low, and the actinic flux inside the cloud is lower than in cloud-free air. Even though the actinic flux may be enhanced slightly inside a water droplet, the enhancement factor is thought to be relatively small, 1.26 to 1.33 (Madronich, 1987; Ruggaber et al., 1997), and therefore easily outweighed by the above effects. In contrast, the rate of oxidation by OH is typically enhanced in the aqueous phase due to high OH concentrations formed from cloud specific processes such as the reaction between  $O_3$  and  $O_2^{\cdot -}$  and the Fenton reaction (Vione et al., 2006). Oxidation of dissolved compounds by OH is typically the most significant oxidation sink and as a first approximation, reaction with other radicals or radical anions may be neglected (Ervens et al., 2003). Comparison of carbonyl lifetimes due to aqueous phase direct photolysis and aqueous phase OH oxidation will reveal the significance of aqueous photolysis in transforming carbonyl compounds dissolved in cloud and fog droplets.

We develop a framework that allows for the prediction of the aqueous photolysis lifetime as a function of wavelength and maximal optical extinction associated with the  $\pi^* \leftarrow n$  transition in carbonyls. Measurements of aqueous quantum yields of atmospherically relevant compounds at actinic wavelengths are rare. In order to understand the range of possible aqueous quantum yields for atmospherically relevant carbonyls, we use published measurements from Encinas et al. (Encinas et al., 1985) of dihydroxyacetone and compare them to the results of semi-quantitative experiments designed to constrain the quantum yield of its structural isomer, glyceraldehyde. These molecules are appropriate surrogates for oxidized water soluble atmospheric organic compounds as they contain both carbonyl and hydroxyl functional groups. Both dihydroxyacetone and glyceraldehyde have large predicted Henry's law constants ( $5.5 \times 10^8 \text{ Matm}^{-1}$  (EPA, 2013) and  $2 \times 10^8 \text{ Matm}^{-1}$  (Saxena and Hildemann, 1996), respectively) and do not hydrate completely in the aqueous phase (fraction unhydrated  $\approx 77\%$  (Glushonok et al., 2003) and  $5\%$  (Glushonok et al., 1986) at  $25^\circ\text{C}$ , respectively). In addition, glyceraldehyde has been identified as a product of isoprene oxida-



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the spectral irradiance was determined with a separate UV-Vis spectrometer (Ocean Optics, USB4000). Both the glyceraldehyde solution and the actinometer solution were continuously mixed during photolysis with a cuvette stirring system (2 Mag-USA). Solutions were kept at 25 °C with a temperature controlled heating/cooling water jacket (Shimadzu). Semi-quantitative measurements of glyceraldehyde concentration (initially 0.1 M) as a function of photolysis time were determined with an Electrospray Ionization Mass Spectrometer (ESI-MS) (Micromass model LCT, resolving power 6000) after derivatization with Girard's reagent T (Acros Organics, 99 %) (Laskin et al., 2012). A solution containing 0.9 mM Girard's reagent T (GT) and 0.05 mM tetraethylammonium chloride (Sigma Aldrich, 98 %) was used to dilute 100 μL aliquots of the reacting glyceraldehyde mixture to 25 mL at several reaction times. Tetraethylammonium chloride is an ideal internal standard as its ionization product has a similar electron affinity and molecular weight to the glyceraldehyde-GT reaction product. The relative concentration of the glyceraldehyde-GT reaction product normalized by the internal standard concentration was tracked as a function of photolysis time.

## 2.2 Modeling approach

The maximum rate of aqueous photolysis relative to the rate of gaseous photolysis for a specific carbonyl compound in an air mass containing liquid water is related to its affinity for the aqueous phase, captured with the Henry's law parameter, and the fraction of the compound that remains in the photolabile un-hydrated form upon dissolution, captured with the hydration equilibrium constant (Epstein and Nizkorodov, 2012).

$$Z = \frac{\frac{dn_{hv}^{\text{gas}}}{dt}}{\frac{dn_{hv}^{\text{aq}}}{dt}} \geq \frac{K_{\text{hyd}} + 1}{(R \cdot T \cdot \text{LWC}_v \cdot K_H)} \quad (1)$$

We define the parameter  $Z$  as the ratio of the rate of photolysis of a specific species in the gas phase and the aqueous phase. For a mono-carbonyl, the maximum value

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of  $Z$  is a function of the hydration equilibrium constant  $K_{\text{hyd}}$ , the ideal gas constant  $R$ , temperature  $T$ , the liquid water content of the air mass  $\text{LWC}_v$  (mass of liquid water per volume of air), and the Henry's law constant  $K_H$ . For di-carbonyls we use a more complicated functional form that takes hydration of the second carbonyl group into consideration (see Supplement). While Henry's law constants (Sander, 1999) and hydration equilibrium constants (Bell and Gold, 1966) were measured for a significant number of simple carbonyls, few measurements exist for more complicated multi-functional molecules.

For effective Henry's law predictions of compounds without published experimental measurements, we employed HENRYWIN v 3.20 (2011), developed by the Environmental Protection Agency and based on methodology described in Hine and Mookerjee (1975) and Meylan and Howard (1991). Experimental measurements were used where possible (Buttery et al., 1971; Sander et al., 2011; Zhou and Mopper, 1990; Staudinger and Roberts, 1996; Betterton and Hoffmann, 1988; Pocker et al., 1969). We used either group or bond contribution estimates for Henry's law predictions. For a specific type of chemical functionality, we employed the method that most accurately reproduced Henry's law measurements of compounds containing the same functionality (typically the lower molecular weight compounds within the specific functional group). However, prediction with group contribution methods may not be possible for small compounds containing multiple functional groups. In these cases, bond estimation methods were employed. We expect some of the scatter in  $K_H$  vs. carbon chain length to be a result of variations in estimation methods. For predictions of hydration equilibrium constants from molecular structure, we used SPARC v4.6 (Karickhoff et al., 2011) based upon work done by Hilal, Bornander and Carreira (Hilal et al., 2005). Experimental measurements of  $K_{\text{hyd}}$  were used where possible (Winkelman et al., 2002; Sham and Joens, 1995; Buschmann et al., 1980; Guthrie, 1978).

After identifying compounds that may have significant aqueous photolysis rates relative to their corresponding gas phase photolysis rates, we investigated if aqueous photolysis rates can compete with the rate of oxidation by dissolved OH.  $Q$  is defined

as the ratio of the rate of oxidation by OH and the rate of direct photolysis in the aqueous phase:

$$Q = \frac{\frac{dn_{\text{OH}}^{\text{aq}}}{dt}}{\frac{dn_{\text{hv}}^{\text{aq}}}{dt}} = \frac{k_{\text{OH}}[\text{OH}]}{J} \quad (2)$$

where  $k_{\text{OH}}$  is the rate constant for reaction with OH in the aqueous phase, [OH] is the concentration of OH, and J is the aqueous photolysis rate constant. Aqueous OH rate constants are published in a comprehensive database by Buxton (Buxton et al., 1988), but do not include many mono- and di-carbonyls. Therefore, we used structure activity relationships from Monod et al. (2005) to estimate aqueous OH rate constants for a variety of carbonyls. These relationships accurately predict rate constants within a factor of five of the measured value for 84 % of the 128 tested compounds in Monod et al. (2005). This method, based on the gas phase OH rate constant structure activity model from Atkinson (Atkinson, 1987; Kwok and Atkinson, 1995), provides a reasonable estimate of OH reactivity based on the reactivity of all hydrogen atoms and the influence of adjacent groups. The training data set does not contain alkenes or cyclic compounds and therefore we do not include these potentially important compounds in our analysis. For acids that dissociate in solution, we used structure activity parameters corresponding to the undissociated acid. The relative fraction of anion and undissociated acid is a function of droplet pH. In order to maintain an upper estimate of the contribution of aqueous direct photolysis, we assume that the acid is completely in its less-reactive undissociated form.

The photolysis rate constant is a function of the absorption cross section,  $\sigma$ , the photolysis quantum yield,  $\Phi$ , and the spectral flux density,  $F_A$ :

$$J = \int F_A(\lambda) \cdot \Phi(\lambda) \cdot \sigma(\lambda) \cdot d\lambda \quad (3)$$

For liquids, absorption cross sections are typically written as extinction coefficients in units of  $\text{M}^{-1}\text{cm}^{-1}$  and are based on  $\log_{10}$  absorbance measurements. To simplify the

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calculations, we assume that the extinction coefficients describing the carbonyl  $\pi^* \leftarrow n$  transition follow a Gaussian dependence on wavelength, which is reflected in previous aqueous extinction coefficient measurements of similar compounds (Malik and Joens, 2000; Bacher et al., 2001):

$$\varepsilon(\lambda) \approx \varepsilon_{\max} \cdot \exp\left[\frac{-4 \cdot \ln(2) \cdot (\lambda - \lambda_{\max})^2}{w^2}\right] \quad (4)$$

where  $\varepsilon_{\max}$  is the maximum extinction coefficient at a wavelength of  $\lambda_{\max}$  and  $w$  is the full width at half maximum obtained from fitting measured extinction coefficient from a data set representing several ketones, aldehydes, along with dihydroxyacetone and glyceraldehyde. We find that  $w = 42$  nm best describes several published extinction coefficients from Xu et al. (1993) and this work. As an approximation, we treat the photolysis quantum yield as an average value over all relevant wavelengths:

$$J = \frac{\langle \Phi \rangle}{N_{AV}} \varepsilon_{\max} \cdot \ln(10) \int F_A(\lambda) \cdot \exp\left[\frac{-4 \cdot \ln(2) \cdot (\lambda - \lambda_{\max})^2}{w^2}\right] d\lambda \quad (5)$$

where  $N_{AV}$  is Avogadro's number. We can then define the lifetime due to photolysis,  $\tau_{hv}$  as:

$$\tau_{hv} = J^{-1} \quad (6)$$

Correspondingly, the lifetime due to oxidation by OH,  $\tau_{OH}$  is:

$$\tau_{OH} = (k_{OH}[\text{OH}])^{-1} \quad (7)$$

Comparison of these lifetimes using the branching ratio,  $Q = \tau_{hv}/\tau_{OH}$ , will indicate compounds that have aqueous photolysis rates that are competitive with aqueous oxidation by OH.

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## 2.3 Computational chemistry methods

We use  $\varepsilon_{\max}$  and  $\lambda_{\max}$  values to estimate aqueous photolysis rate constants. Experimental extinction coefficient measurements of simple carbonyl and dicarbonyl compounds are present throughout the literature. However, extinction measurements of carbonyl compounds found in secondary organic aerosol (SOA) and cloud droplets are less common due to the difficulty in isolating or synthesizing these complex molecules. We performed molecular dynamics simulations to estimate extinction coefficients for several of these atmospherically relevant compounds. All electronic structure calculations were carried out using the TURBOMOLE, version 6.3 quantum chemistry package and employed the SVP basis set (Schafer et al., 1992). Ground state energies and nuclear gradients used in geometry optimizations and molecular dynamics (MD) simulations were computed using the Gaussian basis set implementation of density functional theory (Treutler and Ahlrichs, 1995). Default convergence criteria were used. Geometry optimizations and electronic spectra calculations were done using the hybrid PBE0 (Perdew et al., 1996b) exchange correlation functional. For molecular dynamics (MD) simulations, the PBE (Perdew et al., 1996a) exchange correlation functional was used in combination with the resolution of identity (RI) approximation (Weigend and Häser, 1997). Electronic excitation energies and oscillator strengths were computed using the implementation of time-dependent density functional theory (TDDFT) of TURBOMOLE (Furche and Rappoport, 2005). A total of 4 excited states were computed. To simulate solvent effects of water, we employed the conductor like polarizable continuum method (Klamt and Schurmann, 1993) (COSMO) in the spectra calculations using a dielectric constant of 80.1 (Haynes, 2012). Excitation energies and oscillator strengths were used to simulate an absorption spectra with a normalized Gaussian line shape  $\rho(\lambda)$  for each excitation. We applied a broadening with a full width at half maximum (FWHM) between 0.1–1.5 eV for each band. The absorption spectrum was

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evidence of gaseous carbon monoxide, an expected product of the Norrish type-I splitting. Ethanal, glycolaldehyde, and several unconfirmed products were identified with ESI-MS. A mass spectrum identifying the presence of these products is presented in the Supplement.

Encinas et al. (1985) report that the aqueous quantum yield of dihydroxyacetone at 313 nm is approximately unity, much larger than the value measured for glyceraldehyde. We use this example to stress that quantum yields can vary drastically, even for isomeric compounds with similar functionality. The remarkable difference in quantum yields may be attributed to differences in the chemical mechanism upon exposure to UV light. The dominant step in dihydroxyacetone photolysis is likely cleavage into molecules that do not appreciably combine. However, photolysis of glyceraldehyde may form fragments that subsequently react and revert back to glyceraldehyde.

### 3.2 Role of photolysis in aqueous processing of carbonyls

In view of the large difference between photolysis quantum yields for isomeric compounds, we can only assume that unknown quantum yields of species with products that do not react with the initial species can be anywhere between null and unity. To determine the potential importance of aqueous photolysis processes from the parameters  $Z$  and  $Q$  defined above, we shall assume that  $\Phi = \Phi_{\max} = 1$ . We will also use a cloud liquid water content of  $0.5 \text{ gm}^{-3}$ , typically the largest value routinely measured in the troposphere (Seinfeld and Pandis, 1998; Hobbs, 1993). In certain instances, LWC values of extremely wet clouds can exceed  $0.5 \text{ gm}^{-3}$ , but this typical upper limit provides for a more realistic analysis. The actinic flux is predicted with the Tropospheric Ultraviolet and Visible (TUV) radiation model (Edition 4.4) at a solar zenith angle of  $20^\circ$  with a globally averaged surface albedo of 0.154 from Hummel and Reck (Hummel and Reck, 1979). Figure 2 details the potential significance of aqueous photolysis for a series of compounds with various functional groups on a carbon backbone.

In all molecules, aldehyde, hydroxyl, and carboxyl groups occupy the terminal positions, and keto groups occupy the 2-position in the chain. If two functional groups

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are present, they are positioned on the opposite ends of the chain (e.g., C8 diketone corresponds to octane-2,7-dione). Compounds that lie along the  $Z = 1$  line have aqueous photolysis removal rates that are at most equal to their corresponding gaseous photolysis rates. Removal due to aqueous photolysis should not be important for compounds that lie to the left of the  $Z = 1$  isopleth. For compounds located to the right of the  $Z = 1$  isopleth, aqueous photolysis may be a significant sink depending on the actual unknown photolysis yields and the competition between the reaction with OH and photolysis. Figure 2 graphically illustrates that compounds with low Henry's law constants and large extents of hydration are not appreciably removed by direct aqueous photolysis. Aqueous photolysis is potentially competitive with gaseous photolysis for certain multifunctional carbonyls. For a given family of compounds, increasing the carbon chain length tends to suppress Henry's law constants as the molecules become less polar and thus more hydrophobic.

Atmospheric photooxidation can generate multi-functional, water soluble compounds that contain more than two functional groups. Figure 3 indicates the potential importance of aqueous photolysis from a selection of photolabile organic compounds generated from isoprene photooxidation (Fang et al., 2012) and limonene photooxidation (Jaoui et al., 2006). Several photolabile oxidized compounds have Henry's law constants and hydration equilibrium constants such that aqueous photolysis may be an important sink.

The branching ratio  $Z$  allows us to eliminate compounds that have gaseous photolysis removal rates that exceed aqueous photolysis removal rates ( $Z > 1$ ). However, a low value of  $Z$  does not necessarily imply that photolysis is the primary sink in the aqueous phase as the photolysis lifetime might be too long to be atmospherically relevant and/or it may not be able to compete with oxidation by OH. As in the previous analysis, the lack of experimental aqueous quantum yield measurements prevents us from directly calculating the photolysis lifetime and the branching ratio  $Q$  between the rates of oxidation and photolysis. However, we can assume that  $\Phi = \Phi_{\max} = 1$  in order to calculate the maximum rate of aqueous photolysis compared to aqueous oxidation. Ex-

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perimental extinction coefficients as a function of wavelength are also not available for most compounds, and therefore we parameterize the carbonyl peak as purely a function of  $\varepsilon_{\max}$  and  $\lambda_{\max}$  as described in Sect. 2.2. Aqueous photolysis lifetime at a solar zenith angle of  $20^\circ$  as described with Eqs. (5) and (6) as a function of  $\lambda_{\max}$  and the product  $\langle \Phi \rangle \cdot \varepsilon_{\max}$  is plotted in Fig. 4.

Photolysis lifetime decreases as  $\lambda_{\max}$  and/or  $\varepsilon_{\max}$  increase due to enhanced overlap with the actinic spectrum. Markers indicate the predicted maximum photolysis lifetime ( $\Phi_{\max} = 1$ ) for several carbonyl compounds with published values of  $\lambda_{\max}$  and  $\varepsilon_{\max}$ . Figure 4 illustrates that compounds with large quantum yields will have appreciably short, atmospherically relevant photolysis lifetimes in the aqueous phase. Conjugation can shift the carbonyl peak to the red and increase its intensity (Pavia, 2009), yielding a shorter atmospheric lifetime. One can compare the lifetime of propanal and its ( $\alpha$ ,  $\beta$ ) unsaturated analog – acrolein to investigate this effect. However, in order for removal due to aqueous photolysis to be significant, it must compete with other aqueous processes.

We can compare aqueous photolysis lifetime with lifetime due to aqueous oxidation by OH using Eq. (2). We assume an aqueous OH concentration of  $10^{-13}$  M, reflective of the daytime value recommended in the review by Ervens et al. (2011). This assumed aqueous OH concentration was predicted with theoretical models in Ervens and Volkamer (2010) and Ervens et al. (2003), and is similar to the recommended values in Gelencser and Varga (2005) and Vione et al. (2006). Figure 5 illustrates the competition between these two processes.

Aqueous photolysis is favored for compounds with a slow  $k_{\text{OH}}$ , strong absorption at high wavelengths, and a larger photolysis quantum yields. For compounds that react at the diffusion limit ( $k_{\text{OH}} > 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), aqueous oxidation by OH will exceed aqueous photolysis for all known non conjugated carbonyls because they are typically characterized by  $\lambda_{\max}$  between 260 and 320 nm and  $\varepsilon_{\max} < 25 \text{ M}^{-1} \text{ cm}^{-1}$ . The rate constant for the aqueous oxidation by OH radical has to be lower than  $k_{\text{OH}} = 10^{8.5} \text{ M}^{-1} \text{ s}^{-1}$  in order for the direct photolysis to be competitive.

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We can compare the maximum rate of aqueous photolysis ( $\Phi_{\max} = 1$ ) with the rate of aqueous oxidation by OH radical with help of rate constant predictions using structure activity coefficients. All predicted rate constants were capped at the diffusion controlled limit of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (Vione et al., 2006). Complete extinction coefficients across all actinic wavelengths were not available for most compounds, but published values of  $\lambda_{\max}$  and  $\epsilon_{\max}$  are available for many carbonyl compounds (Xu et al., 1993; Malik and Joens, 2000; Steenken et al., 1975; Hammond et al., 1959; Mackinney and Temmer, 1948; Schutze and Herrmann, 2004; Rice, 1920; Gubina et al., 2004). For simple mono- and di-carbonyl compounds without published  $\lambda_{\max}$  and  $\epsilon_{\max}$  values, we made educated upper-estimates based on the values of compounds with similar functionality. In order to determine the compounds that may be significantly removed with aqueous photolysis, we also must consider the magnitude of the branching ratio  $Z$  in our analysis. Specifically, aqueous photolysis is only potentially important for compounds with  $Z < 1$  (the rate of removal due to aqueous photolysis is potentially greater than the rate of removal due to aqueous oxidation by OH radical) and  $Q < 1$  (the rate of removal due to aqueous photolysis is potentially greater than the rate of removal due to gaseous photolysis).

Figure 6 illustrates both of these branching ratios for the same series of carbonyl compounds presented in Fig. 2 at a solar zenith angle of  $20^\circ$  in an air mass with a liquid water content of  $0.5 \text{ gm}^{-3}$  at  $25^\circ \text{C}$ . Reproductions of Fig. 6 under other relevant atmospheric conditions are presented in the Supplement. The upper right quadrant of Fig. 6 contains molecules for which aqueous photolysis is slower than both gaseous photolysis and aqueous oxidation by OH. The upper left quadrant contains molecules for which aqueous photolysis may be faster than gaseous photolysis, but removal by OH is still the dominant sink in the aqueous phase. The lower left quadrant containing pyruvic acid, 3-oxobutanoic acid, 3-oxopropanoic acid are compounds that aqueous photolysis may be faster than both gaseous photolysis and aqueous oxidation by OH. The lower right quadrant containing 3-oxopropanoic acid, 2,3-butanedione, and

oxoacetic acid consists of molecules that may have aqueous photolysis rates that are faster than aqueous oxidation by OH, but gaseous photolysis is the dominant sink.

In this series of carbonyl compounds, only pyruvic acid, 3-oxobutanoic acid, and 3-oxopropanoic acid may be preferentially removed by aqueous phase photolysis. These compounds have sufficiently high Henry's law constants, do not hydrate completely in the aqueous phase, and have predicted  $k_{\text{OH}}$  values significantly less than the diffusion controlled limit ( $7.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $7.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and  $5.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively).

### 3.3 Computational chemistry predictions of spectroscopic properties

To predict the importance of aqueous photolysis for compounds where no spectroscopic data is available, we compute the vibronic absorption spectrum using time-dependent density functional theory (TDDFT). To assess the accuracy of this approach we computed the absorption spectra of several reference molecules in the gas phase and in solution (Table 1). Only the relevant absorption band (the band closest to 280 nm) is reported. In cases where two peaks were present in the 280 nm region, both values were reported. Single point values (SP) have been computed using the ground state equilibrium geometry with a fixed Gaussian broadening of 0.1 eV. For some compounds, with this applied broadening, we get more fine structure than found in the published experiments. If a different broadening has been used to achieve better agreement with the experiment, the value is given in parenthesis. MD denotes that the spectra have been computed by averaging over several structures obtained from MD simulations. A comparison of the acetone aqueous and gas phase spectrum is presented in Fig. 7. The computed spectra over all relevant wavelengths are presented in the Supplement.

Two different approaches were employed. Firstly, we calculated TDDFT excitation energies and oscillator strengths using the equilibrium ground state geometries. Secondly, to assess the influence of the nuclear vibrations on the excitation energies and oscillator strengths the TDDFT results were averaged over an ensemble of structures obtained from ground state BOMD.  $\lambda_{\text{max}}$  values for the gas phase are similarly ac-

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curate for single point (SP) calculations and MD calculations, exhibiting mean absolute errors (MAE) of 14.4 and 15.4 nm, respectively. In solution, MAE amount to 14.8 and 17.0 nm for SP and MD calculations, respectively. Comparing the extinction coefficients of SP calculation with MD simulations, we notice that extinction coefficients are strongly underestimated by the SP calculations, irrespective of the broadening. This is attributed to the neglect of vibrational effects in SP calculations. These effects can be particularly strong for small symmetric systems such as acetone or 2,3-butanedione. The symmetry breaking occurring during MD is necessary to predict extinction coefficients accurately (Table 1). 3-oxobutanal appears to be an outlier – the MD calculations largely overestimate extinction coefficients (experimental  $\epsilon_{\max} = 10 \text{ L mol}^{-1} \text{ cm}^{-1}$  (Martinez et al., 1975); calculated  $\epsilon_{\max} = 306.7 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), and the SP value ( $75 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) is also too high. For the SP values with individually adjusted Gaussian broadening, we find an MAE of  $35.6 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The MAE of the MD calculations is significantly smaller ( $15.2 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) using a constant broadening of 0.1 eV. In summary, with the exception of 3-oxobutanal we obtain reasonable accuracy for both,  $\lambda_{\max}$  and  $\epsilon_{\max}$  values, for symmetric and non symmetric molecules using MD.

We chose this method to compute the spectra of several relevant photolabile compounds identified in d-limonene (Jaoui et al., 2006) and isoprene (Fang et al., 2012) SOA. These four carbonyl-containing compounds, 4-hydroxy-3-methyl-but-2-enal, 3,6-oxoheptanoic acid, ketolimononaldehyde, and ketonorlimonic acid do not have published aqueous extinction coefficients. Computationally derived spectra and  $\epsilon_{\max}$  and  $\lambda_{\max}$  values are presented in the Supplement. We find that only 3,6-oxoheptanoic acid has both  $Q$  and  $Z$  values that are less than unity. ( $Q = 0.13$  and  $Z = 2.1 \times 10^{-5}$ ) These oxygenated molecules have large Henry's law constants that lead to small values of  $Z$ . However, only 3,6-oxoheptanoic acid has a large enough absorption cross section to overcome the competing rate of oxidation by OH radical. A reproduction of Fig. 6 containing these compounds is presented in the Supplement. We advise caution

when using results derived from the molecular dynamics simulations as there is a large uncertainty in the computed  $Q$  values.

#### 4 Atmospheric implications

Aqueous photolysis is not likely to be a significant atmospheric sink of the relatively simple carbonyls investigated in this manuscript. There are important exceptions to this rule including pyruvic acid, 3-oxobutanoic acid, and 3-oxopropanoic acid; we note that aqueous photolysis experiments of pyruvic acid are well established in the literature, see Refs. (Leermakers and Vesley, 1963; Larsen and Vaida, 2012; Guzmán et al., 2006, 2007). While carbonyls, keto-carboxylic acids, and hydroxyl-carbonyls may readily partition into cloud and fog droplets, once in the aqueous phase, oxidation by hydroxyl radicals is a more efficient removal process than direct photolysis. OH oxidation rate constants typically increase for larger compounds as there are more hydrogen atoms available for abstraction. The same functional groups that allow for photolysis at actinic radiation and increased solubility in water can also increase the rate of hydrogen abstraction in the molecule. Only photolabile carbonyls with enough oxygen functionality to enhance solubility but few hydrogen atoms for abstraction by OH may have significant rates of aqueous photolysis.

Our assertion that the direct photolysis of aqueous carbonyls is generally insignificant may break down in specific cases. Certain molecular functionalities that we have not fully investigated could enhance the rate of aqueous photolysis. Conjugation with  $C=C$  double bonds can shift the carbonyl  $\pi^* \leftarrow n$  transition peak to the red and increase intensity (Pavia, 2009). For example, the types of multifunctional carbonyls found in secondary organic aerosols must have sufficiently high values of  $\epsilon_{\max}$  because they are readily degraded by direct photolysis. Aqueous photolysis of highly oxygenated aromatic carbonyls may also be important (e.g., for benzaldehyde:  $\lambda_{\max} \approx 283$ ,  $\epsilon_{\max} = 1550 \text{ M}^{-1} \text{ cm}^{-1}$ , Sham and Joens, 1995).

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Our analysis assumed a SZA of  $20^\circ$  and a relatively large LWC. Irradiation at a higher solar zenith angle of  $0^\circ$  will not significantly affect the results of our analysis. However, cloud and fog droplets with a depleted OH concentration will enhance the relative contribution of aqueous photolysis processes. If we calculate the branching ratio  $Q$  with  $C_{\text{OH}} = 2.5 \times 10^{-14}$  M, the lower end of the fair weather cloud OH concentration suggested in Ref. in Vione et al. (2006), we find that aqueous photolysis of 4-oxopentanoic acid and 5-oxohexanoic acid may become important in addition to pyruvic acid, 3-oxobutanoic acid, and 3-oxopropanoic acid (see Supplement Fig. S6). However this depressed aqueous OH radical concentration is unlikely to occur at high SZA when both photolysis and production of OH should be enhanced. Perturbations from Henry's law equilibrium are possible (Finlayson-Pitts and Pitts, 2000; Li et al., 2008; van Pinxteren et al., 2005) and can be interpreted in a shift in the horizontal axis in Fig. 6. Each order of magnitude enhancement in the aqueous phase concentration of the selected species above the Henry's law equilibrium value will shift its marker one unit to the left. For example, if aqueous phase concentration is enhanced by a factor of 100 over the equilibrium value, aqueous photolysis of methyl glyoxal becomes a potentially important chemical sink. However, perturbations from Henry's law will not affect the behavior of compounds where  $\log_{10}(Q) > 0$  as the competition between aqueous phase oxidation by OH and aqueous photolysis will remain unchanged.

As information on the common carbonyl constituents of particulate matter, clouds droplets, and fog droplets becomes available, the question of the dominant atmospheric fate of these compounds will invariably arise. With limited information about a specific compound (estimates of  $K_{\text{H}}$ ,  $k_{\text{hyd}}$ ,  $\lambda_{\text{max}}$ , and  $\varepsilon_{\text{max}}$ ), this framework will be a useful tool to determine if quantum yield experiments will produce pertinent results, or should even be carried out in the first place.

Supplementary material related to this article is available online at:  
[http://www.atmos-chem-phys-discuss.net/13/10905/2013/  
acpd-13-10905-2013-supplement.pdf](http://www.atmos-chem-phys-discuss.net/13/10905/2013/acpd-13-10905-2013-supplement.pdf).

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**Table 1.** Calculated maximum absorption wavelength  $\lambda_{\max}$  (nm) and decadic molar absorption coefficients  $\varepsilon_{\max}$  ( $\text{L mol}^{-1} \text{cm}^{-1}$ ) of the reference compounds.

		$\lambda_{\max}$ [nm]			$\varepsilon_{\max}$ [ $\text{L mol}^{-1} \text{cm}^{-1}$ ]		
		SP calculated	MD calculated	Exper.	SP calculated	MD calculated	Exper.
acetone	Gaseous	283	252	275	0.04	10.9 (0.4 eV)	5.0
	Aqueous	273	243	281	0.02	8.5 (0.4 eV)	13.7
levulinic acid	Gaseous	279	282	n.a.	13.9	97.4	n.a.
	Aqueous	271	281	270	13.9	54.7	25.1
2-oxopropanal	Gaseous	279	283/298	280	6.1	13.0/12.5	12.8
	Aqueous	281	276/291	284	6.2	24.8/27.1	16
3-oxobutanal	Gaseous	289	285/305	247	37.1 (1.5 eV)	91.3/310.1	n.a.
	Aqueous	281	278/302	280	75.6 (0.7 eV)	130.9/306.7	10
2,3-butanedione	Gaseous	275	278	271	0.2	5.0	13.1
	Aqueous	269	271	284	0.3	12.0	26.3
pyruvic acid	Gaseous	237	252	254	44.7 (0.2 eV)	20.9	4.2
	Aqueous	229	243	290	88.9	25.7	15.7
glyceraldehyde	Gaseous	274	275	n.a.	423.5	158.1	n.a.
	Aqueous	268	268	271	64.2 (0.6)	136.9	3.7

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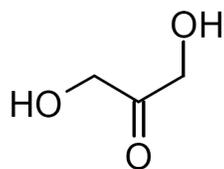
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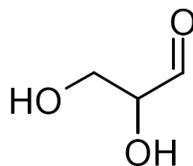
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**Dihydroxyacetone**  
(1,3-Dihydroxypropan-2-one)



**Glyceraldehyde**  
(2,3-Dihydroxypropanal)

**Fig. 1.** Chemical structures of dihydroxyacetone and glyceraldehyde.

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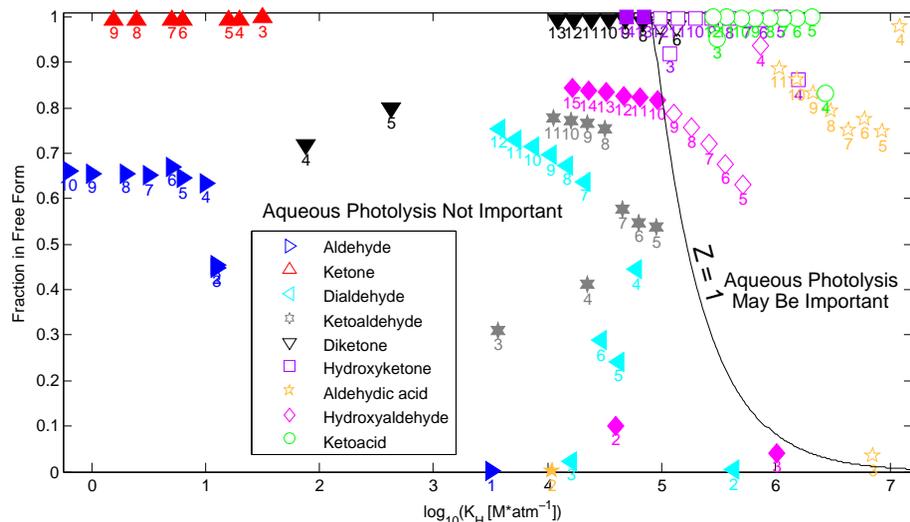
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**Fig. 2.** Henry's law constants as a function of hydration equilibrium for linear-chain compounds in an air mass with a liquid water content of  $0.5 \text{ gm}^{-3}$ . Numbers below the symbols indicate the total number of carbon atoms in the molecule. Hydration equilibrium constants and Henry's law constants are obtained from experimental data or computational predictions as explained in Sect. 2.2. Molecules denoted by filled shapes have gaseous photolysis rates that exceed the aqueous photolysis rates. Unfilled shapes to the right of the  $Z = 1$  line indicate that specified molecules may have aqueous photolysis rates that exceed gas phase photolysis rates.

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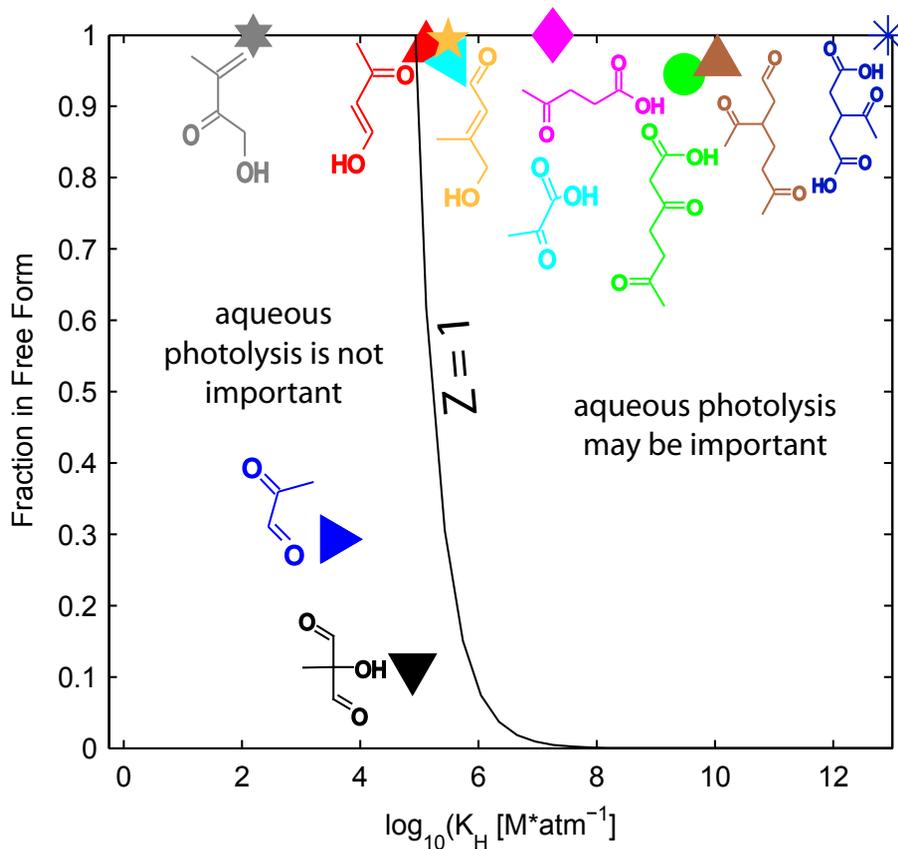
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**Fig. 3.** Hydration equilibrium vs. Henry's law constants for photolabile compounds formed from isoprene (Fang et al., 2012) and limonene (Jaoui et al., 2006) photooxidation.

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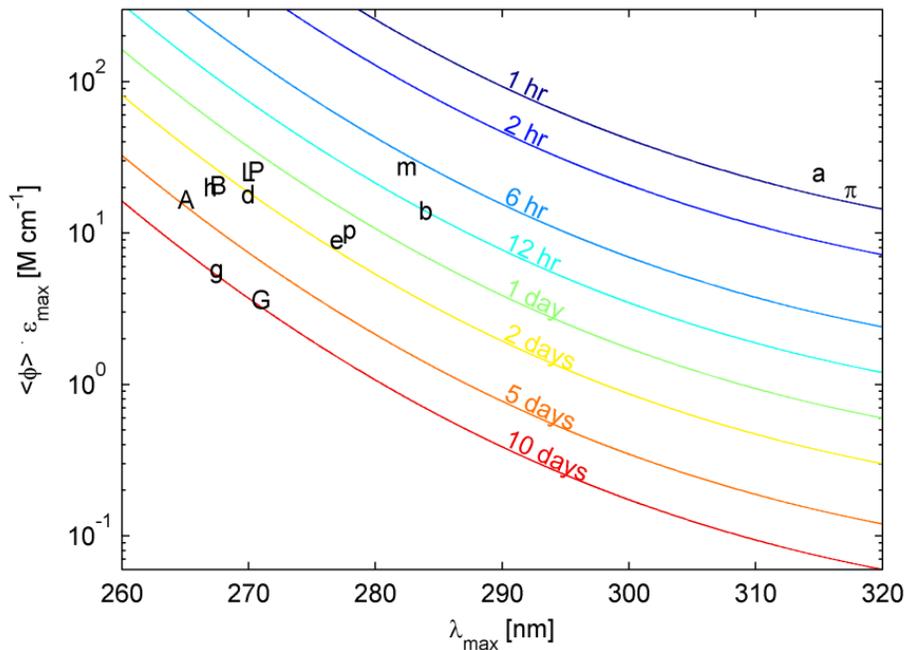
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## Direct photolysis of carbonyl compounds

S. A. Epstein et al.



**Fig. 4.** Predicted aqueous photolysis lifetimes as a function of the wavelength of maximum absorbance of the carbonyl peak and the product of the average photolysis yield and the maximum extinction coefficient of said peak at a solar zenith angle of  $20^\circ$ . Arabic and Greek letters indicate the minimum photolysis lifetime (when photolysis yield is unity) for the following compounds: e) ethanol, p) propanal, b) butanal, A) acetone, B) butanone, P) 2-pentanone, m) methyl glyoxal, g) glyoxal, L) levulinic acid, h) hydroxyacetone, d) dihydroxyacetone, G) glyceraldehyde,  $\pi$ ) pyruvic acid, a) acrolein. Marker positions are determined by experimental values of  $\lambda_{\max}$  and  $\varepsilon_{\max}$ .

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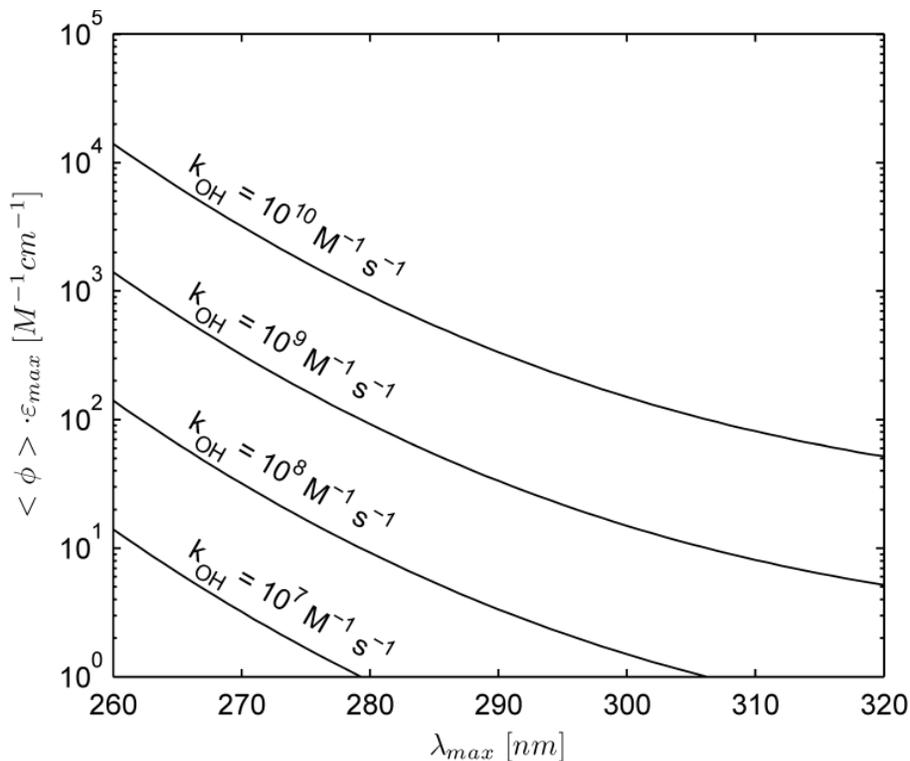
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## Direct photolysis of carbonyl compounds

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**Fig. 5.** Comparison of aqueous photolysis at a solar zenith angle of  $20^\circ$  and aqueous oxidation by OH at a typical concentration of  $10^{-13}$  M. For a compound with a  $k_{OH}$  corresponding to the isopleths, molecules with values of  $\lambda_{max}$  and  $\varepsilon_{max} \cdot \langle \Phi \rangle$  that are below the isopleth will be preferably removed with oxidation by hydroxyl radicals. Conversely, molecules with values of  $\lambda_{max}$  and  $\varepsilon_{max} \cdot \langle \Phi \rangle$  that are above the isopleth will be preferably removed by aqueous photolysis.

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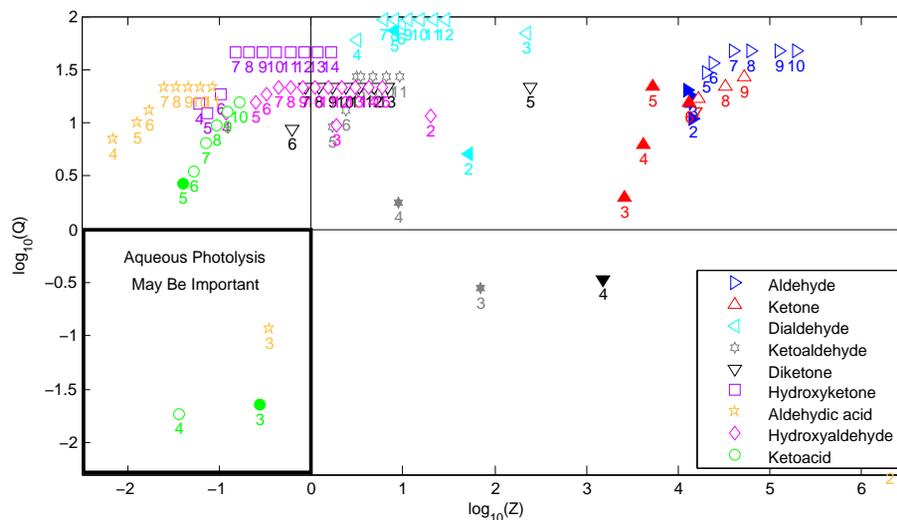
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## Direct photolysis of carbonyl compounds

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**Fig. 6.** Branching ratio between aqueous oxidation by OH radicals and aqueous photolysis ( $Q$ ) vs. branching ratio between gaseous photolysis and aqueous photolysis ( $Z$ ) for the series of compounds presented in Fig. 2 in an air mass with  $LWC = 0.5 \text{ gm}^{-3}$  at a solar zenith angle of  $20^\circ$ . All aqueous quantum yields are assumed to be at their upper limit. Molecules notated with filled markers indicate that published  $\lambda_{\text{max}}$  and  $\varepsilon_{\text{max}}$  values were used to calculate extinction coefficients (see Supplement). Open markers indicate that extinction coefficients were determined with estimations of  $\lambda_{\text{max}}$  and  $\varepsilon_{\text{max}}$  from compounds with similar functional groups. Numbers corresponding to each symbol indicate the number of carbon molecules in the chain.

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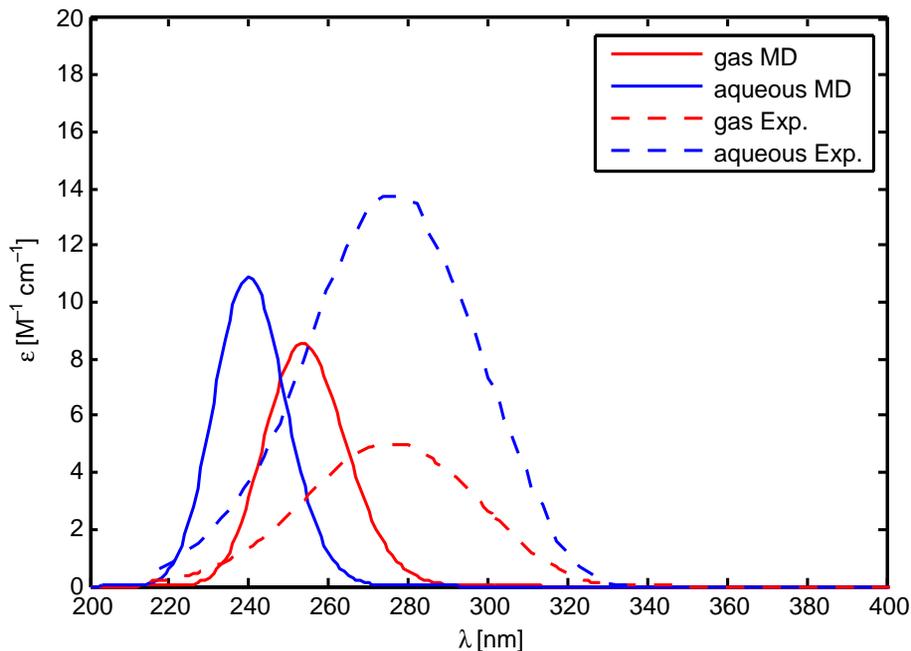
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## Direct photolysis of carbonyl compounds

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**Fig. 7.** Comparison of published aqueous (Calvert and Pitts, 1966) and gas phase acetone spectra (Sander et al., 2011) with spectra calculated using MD simulations. We employed a Gaussian broadening of 0.4 eV to achieve the best agreement with experiment.

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