Davide Vione, Claudio Minero,
Valter Maurino
Dipartimento di Chimica Analitica
Università di Torino
davide.vione@unito.it

SURFACE PHOTOCHEMISTRY IN THE ATMOSPHERIC AQUEOUS PHASE

Photochemical processes play an important role in the atmospheric aqueous phase. Photoinduced reactions at the air-water interface have been the object of much attention, because different kinds of surface effects could considerably enhance the reaction rates. Furthermore, many organic compounds are known to undergo accumulation at the air/water interface, and some of them can also interact with inorganic ions. Potentially very important is also the enhancement of the photolysis quantum yields at the interface, where photoactive molecules are surrounded by an incomplete solvent cage.

Photochemical processes play an important role in the transformation of organic compounds in the atmosphere. These reactions control the atmospheric lifetime of many species, including harmful pollutants and climate-forcing gases [1]. The relevant reactions can take place in the gas phase, inside or at the surface of water droplets, and on airborne particulate matter. They can consist of direct or indirect photolysis processes [2]. In direct photolysis a sunlight-absorbing compound undergoes bond breaking (reaction 1) or photoionisation (reaction 2) upon photon absorption [3]:

$$\text{A-B} + h\nu \rightarrow \text{A}^{\bullet} + \text{B}^{\bullet} \quad (1)$$

$$\text{A-B} + h\nu \rightarrow \text{A-B}^{+\bullet} + e^{-} \quad (2)$$

Concerning direct photolysis on particulate matter, an interesting finding has been that black carbonaceous particles absorb sunlight and can protect adsorbed compounds from photodegradation. Accordingly, the relevant phototransformation kinetics is significantly faster on white substrates such as silica and alumina, compared to darker compounds such as Fe oxides and carbonaceous material [4].

Indirect photolysis takes place in the presence of photosensitisers that absorb sunlight and produce reactive species that can induce the transformation of other molecules. The latter do not necessarily need to absorb solar radiation. Photogenerated reactive species can be the excited triplet states of aromatic ketones, of quinones, and of polyaromatic compounds, singlet oxygen ($^1O_2$) [5, 6], and reactive radicals formed upon photolysis of the sensitisers [7]. In the case of the excited triplet states and of singlet oxygen, reactions (3-7) would involve the sensitiser S, oxygen, and an organic substrate M, where the superscripts ^{S1} and ^{T1} indicate the first excited singlet and triplet states, respectively [8, 9]:

Tab. 1 - Relative contribution of the photolysis of H_2O_2, NO_3^-, NO_2^-, HNO_2 and Fe(III) to the photochemical generation of $^{\bullet}OH$ in typical continental clouds [7]. The reference is the contribution of Fe(III), taken as 1.0

Species	Concentration, M	Contribution to $^{\bullet}OH$, relative to Fe(III)
H_2O_2	5.8×10^{-5}	9.8
NO_3^-	3.1×10^{-4}	4.2
NO_2^-	1.9×10^{-7}	0.05
HNO_2	1.0×10^{-8}	0.05
Fe(III)	5.0×10^{-7}	1.0

$$S + h\nu \rightarrow S^{S1} \quad (3)$$

$$S^{S1} \xrightarrow{\text{(inter-system crossing)}} S^{T1} \quad (4)$$

$$S^{T1} + O_2 \rightarrow S + {}^1O_2 \quad (5)$$

$$M + {}^1O_2 \rightarrow \text{Products} \quad (6)$$

$$S^{T1} + M \rightarrow \text{Products} \quad (7)$$

Transformation reactions would take place on the surface of organic particles and in water droplets (mist, fog, cloud), where many important organic components (quinones, aromatic carbonyls, furans) are known photosensitisers [5, 6]. Moreover, humic and fulvic substances play a major role in inducing photosensitised reactions in river and lake water [10], and somewhat similar compounds (Humic-Like Substances, HULIS) are also present in atmospheric aerosol, fog and cloud [11]. The possible photochemical properties of HULIS are completely unknown at the moment and would deserve dedicated studies.

As far as the role of reactive radical species is concerned, in the gas phase the most important ones are $^{\bullet}OH$ and $^{\bullet}NO_3$. The radical $^{\bullet}OH$ also occurs in the atmospheric aqueous phase, because of transfer from the gas phase, reaction between O_3 and $O_2^{-\bullet}$, the Fenton reaction ($Fe^{2+} + H_2O_2$), and photochemical processes such as the photolysis of hydrogen peroxide, nitrate, nitrite, nitrous acid, and Fe(III) hydroxocomplexes [7]. Tab. 1 reports the relative contribution of the photochemical sources to $^{\bullet}OH$ photogeneration under conditions typical of continental clouds, in the presence of 0.5 μM Fe(III).

The scenario can be significantly different under more polluted conditions. In the case of fog water from California's Central Valley the concentration of NO_2^-/HNO_2 reached up to 6×10^{-5} M, while nitrate had a maximum value of 3×10^{-3} M. Under these circumstances the photolysis of NO_2^-/HNO_2 accounted for 50-100% of $^{\bullet}OH$ photoproduction [12].

The occurrence of the radical $^{\bullet}NO_3$ in atmospheric waters would mainly be accounted for by transfer from the gas phase [13], but other reactive species can be formed upon photolysis in solution. Examples are $^{\bullet}NO_2$, formed upon nitrate photolysis or nitrite photooxidation [14, 15], $Cl_2^{-\bullet}$, produced by chloride oxidation or by the UV photolysis of the complex $FeCl^{2+}$ [16, 17], and $Br_2^{-\bullet}$, deriving from bromide oxidation or $FeBr^{2+}$ photolysis [18].

The relative importance of gas vs. aqueous-phase degradation processes depends on many factors, among which the liquid water content of the atmosphere, the partitioning of a given compound between the gas phase and the aqueous solution, and the reactivity of the compound in each phase. As far as the latter issue is concerned, consider for instance the reaction of 2-propanol with $^{\bullet}OH$ in the gas phase (10^6 (molecules $^{\bullet}OH$) cm^{-3} on average) and in solution (average $[^{\bullet}OH] = 2\times10^{-14}$ M) [19, 20]. From the reported reaction rate constants [21, 22], the atmospheric lifetime of 2-propanol would be 2 days in the gas phase and only 7 hours in water droplets. For phenol the corresponding lifetimes would be 10 hours and 1 hour, respectively. Reactivity in water droplets could therefore be very important for the compounds that undergo efficient partitioning in the aqueous phase and can be transformed quickly in that compartment.

The importance of photochemical reactions in atmospheric water droplets would be influenced, and possibly enhanced, by some additional factors. They are the light-field distribution inside the droplets, the accumulation at the air-water interface of surface-active compounds, the surface co-adsorption of organic and inorganic species, and the enhanced photolysis quantum yields because of the incomplete solvent cage at the air/water interface. These issues could influence both the reaction rates in the whole droplet, and the rate distribution in the droplet volume. The different effects that could increase the photoinduced reaction rates inside droplets and at the droplet surface are discussed in the paragraphs that follow.

Actinic flux in water droplets

Atmospheric waters modify significantly the flux of sunlight because of different phenomena. Clouds as well as aerosols are able to scatter and absorb radiation. As a consequence, the sunlight intensity is considerably increased on top of clouds and is usually reduced inside and below them [23, 24]. This fact leads to a non-homogeneous distribution of the photochemical reaction rates inside the cloud. Understandably, photochemical processes would be favoured in the top layer and inhibited in the bottom one [25], but no average enhancement of cloud photochemistry can be expected because of this phenomenon.

However, spherical (or almost spherical) droplets are also able to refract and diffract the incident light. Incident radiation in a spheri-

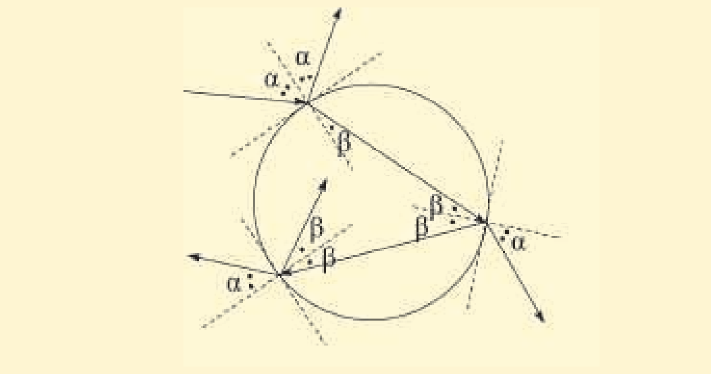

Fig. 1 - Multiple reflection/refraction phenomena at the air-water interface of a spherical droplet. It is $\sin\alpha = n\sin\beta$, with n=1.33-1.37 depending on the wavelength of the incident beam. Three events only are shown, but further ones would take place until the intensity of the light beam in the droplet vanishes because of absorption and refraction

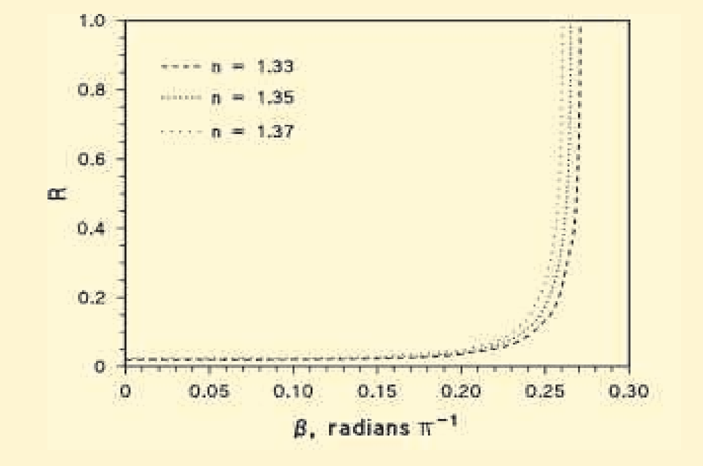

Fig. 2 - Fraction R of reflected radiation in a water droplet, as a function of the angle β and the refraction index n. Note that 0.25 on the X-axis scale means 1/4 π in radians units

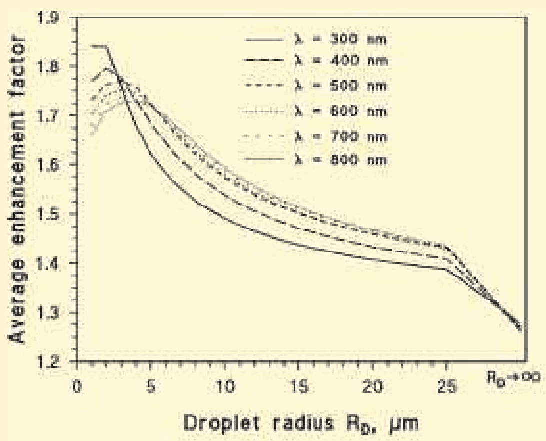

Fig. 3 - Average enhancement factor η of the irradiation intensity in water droplets, compared to the surrounding gas phase, as a function of the droplet radius RD and the radiation wavelength λ

cal droplet can be reflected and refracted at the air-water interface, because the refraction index n of water is in the 1.33-1.37 range between 800 and 300 nm. Due to the spherical symmetry, a series of reflection/refraction events would take place (see Fig. 1), which increase the effective path length of the radiation in the droplet and therefore the probability of photon absorption by the dissolved compounds [26-28].

A fraction 1-R of the incident radiation from the gas phase will therefore enter the droplet, and at each successive contact with the interface a fraction R will be reflected back into the water phase. Within successive reflections the radiation can be absorbed by the dissolved molecules. Fig. 2 reports the trend of R as a function of the angle β, for n=1.33-1.37. Note that the highest value of β that is possible inside a spherical water droplet is 0.26-0.27 π (47-49°), corresponding to $\alpha=\pi/2$ (90°).

A fraction of the incident radiation from the gas phase will remain inside the droplet till it is absorbed, and a part will be lost by refraction back into the gas phase. On average, the multiple reflections will increase the absorbed photon flux by a dissolved molecule M compared to the case where M is in the gas phase. The phenomenon is equivalent to an enhancement of the intensity of the radiation field inside the droplets compared to the surrounding gas phase. The ratio between the intensity inside the droplet, calculated given the reported assumptions, and that in the gas phase is the actinic flux enhancement η [26].

The applicability of the laws of optical geometry depends on the ratio between the droplet size and the radiation wavelength, usually measured by the size parameter $x=2\pi R_D\lambda^{-1}$, where R_D is the droplet radius, and λ the radiation wavelength [29]. For cloud droplets with R_D=10 μm, and λ in the 300-600 nm range, a size parameter x=100-200 suggests that the optical geometry would just be a rough approximation. The exact treatment should consider the wave description of light and apply the Mie theory of refraction. The calculation of the actinic flux enhancement η can be carried out numerically by means of the appropriate codes, and the resulting values depend on both the radius of the droplet and the radiation wavelength [30, 31]. Understandably, the η values derived from the Mie theory ($\eta(R_D,\lambda)$) tend to the optical geometry one ($\eta(\lambda)$) at large R_D, when the droplet size is much higher than the radiation wavelength.

Fig. 3 reports the value of η as a function of the droplet radius R_D for different values of the irradiation wavelength λ, according to the Mie theory of refraction. The radiation of lower wavelength, which is more relevant to photochemical processes, shows more significant changes of η as a function of R_D [26].

Another interesting effect connected with the Mie theory is the light-field distribution inside the droplet [32]. The relative intensity at the surface can be considerably enhanced compared to the bulk in the equatorial plane of the droplet (see Fig. 4a), but in other spherical sections the surface intensity is lower than in the bulk (Fig. 4b,c). The data of Fig. 4 are referred to an environmentally significant irradiation spectrum of 290-600 nm, and R_D=1 μm [33]. The absolute values of the average intensity are dependent on the irradiation wavelength, but the general framework would not change dramatically if a different spectrum is considered.

On average over the different droplet planes, the irradiation intensity in the surface layer would not be higher than in the bulk. Actually, in a 1 μm water droplet the irradiation intensity at the surface in the 290-600 nm interval would be about 20% lower than in the bulk [33].

Surface accumulation and co-adsorption phenomena

Many solutes are able to undergo accumulation at the air-water interface of atmospheric droplets, because of different processes. Amphiphilic compounds, such as fatty acids, dicarboxylic acids and some fractions of HULIS are well known to show significant surface activity. They can reach much higher concentration at the air-water interface compared to the solution bulk [34, 35].

Surface accumulation is also operational for hydrophobic species such as aliphatic and aromatic hydrocarbons. They undergo poor solvation by the water molecules and tend to be "pushed" at the interface, where the incomplete solvent cage would make interaction with water energetically less expensive. In the case of aromatic hydrocarbons, the surface accumulation would increase with molecular size in the order benzene<naphthalene<anthracene [36]. For these compounds, surface accumulation would be an important phenomenon in the process that finally leads to volatilisation [37]. An increase of the interface concentration is also predicted for dissolved gases and small, neutral molecules and radicals such as N_2, O_2, O_3, $^{\bullet}OH$, $HO_2^{\bullet}$, and H_2O_2. All these species show in fact a free-energy minimum at the surface [38].

Recent studies indicate that the phenomenon of surface accumulation can also involve ionic species, depending on their interaction with water molecules and their polarisability. Among the anions that can undergo surface accumulation there are the halides, with the exception of fluoride, in the order $Cl^- < Br^- < I^-$, and this feature could have important consequence on the chemical and photochemical reactions that occur in sea-salt droplets and aerosols [39, 40]. The surface accumulation of chloride plays a significant role in the processes of uptake of reactive gas species and radicals (e.g. O_3, H_2O_2, $^{\bullet}OH$), with subsequent possible oxidation of chloride to photochemically active compounds such as Cl_2 and HClO [41].

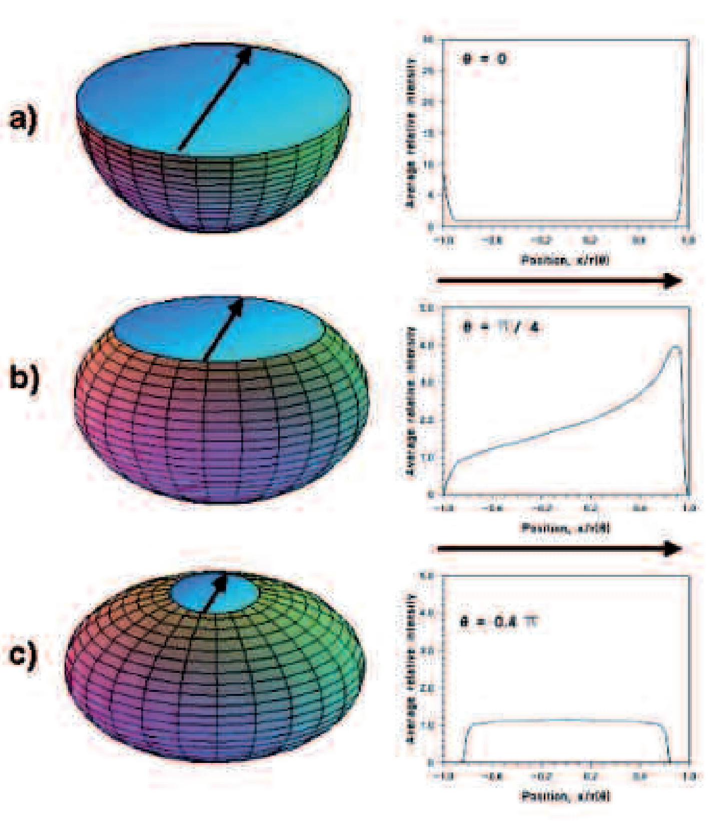

Fig. 4 - Light-field intensity (averaged over the 290-600 nm wavelength interval) in different sections of a spherical water drop (R_D=1 μm). Each section is graphically depicted. The arrows represent both the direction of illumination and the path along which the average irradiation intensity is calculated. θ is the angle between the centre of the sphere and the relevant section

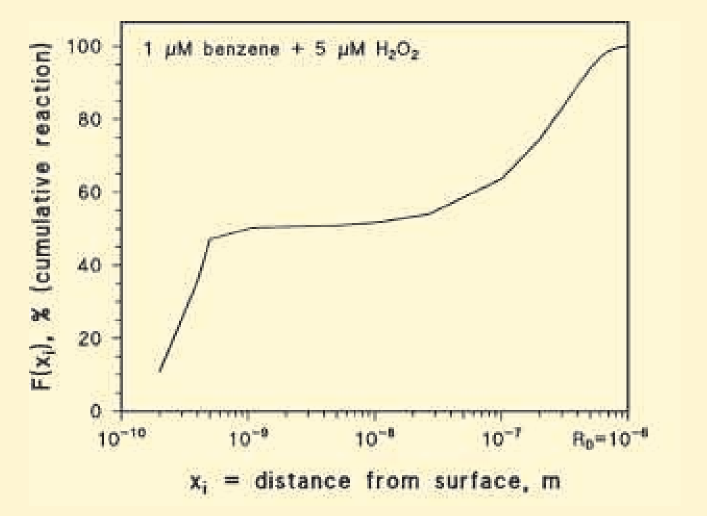

Fig. 5 - Trend of F(xi), expressed as percentage, as a function of the distance from the droplet surface (surface: x_i=0; centre: x_i=R_D, the droplet radius)

The surface accumulation of hydrophobic species and of photoactive compounds could co-operate in the enhancement of the photochemical reactions at the interface. For instance, hydrogen peroxide has a slight preference for the droplet surface layer, where it can be present at double concentration compared to the bulk [38]. Benzene would undergo much higher surface accumulation. Experimental data indicate that, in the presence of 1 μM bulk benzene, the concentration in the surface layer would be increased by a factor of 400 compared to the bulk. The thickness of such a layer would be just 0.5 nm, beyond which the concentration of benzene would rapidly fall down to the bulk value. Accordingly, for calculation purposes the distribution of benzene inside the droplet can be assumed as a slab profile with a concentration of 0.4 μM in the first 0.5 nm from the surface, and 1 μM at higher distance [37]. Note that a concentration of 1 μM is representative of the levels of many toxic aromatic compounds in polluted areas [20].

The interface accumulation of hydrogen peroxide is likely to involve a thin layer as well, and for sake of simplicity it can be hypothesised that the two layers have equal thickness. A bulk concentration $[H_2O_2]$ = 5 μM would be representative of atmospheric water in polluted areas [42].

The photolysis of hydrogen peroxide yields $^{\bullet}OH$ radicals (reaction (8) [43]), which can react with benzene to give phenol with 95% yield [44]:

$$H_2O_2 + h\nu \rightarrow 2\,^{\bullet}OH \qquad (8)$$

At 5 μM bulk H_2O_2, and the small optical path lengths that are typical of atmospheric droplets, the photon flux absorbed by hydrogen peroxide (moles of photons $L^{-1}s^{-1}$ units) would be directly proportional to $[H_2O_2]$. The rate of photolysis, which is the product of the absorbed photon flux times the photolysis quantum yield, would be proportion-

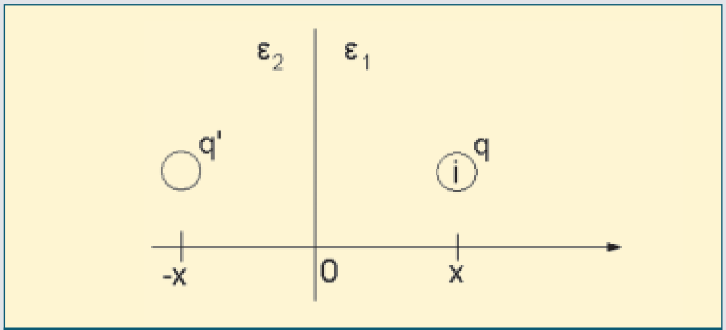

Fig. 6 - Schematic of the ion i (charge q) and of its image charge q', symmetric relative to the air-water interface. The position of the interface corresponds to the origin of the x axis. ε_1 and ε_2 are the dielectric constants of the two media (1=water, 2=air)

al to $[H_2O_2]$ as well [42]. Additionally, benzene or otherwise another aromatic compound at typical atmospheric concentration values would not be the main $^{\bullet}$OH scavenger in water droplets; compounds such as formate and formaldehyde would generally play the main role [45, 46]. As a consequence, the formation rate of phenol (r_{Phenol}) would also be directly proportional to [Benzene]. One gets $r_{Phenol} \propto [Benzene][H_2O_2]$, which varies with the distance from the droplet surface following the distribution of the two species.

Fig. 5 reports the cumulative reaction $F(x_i)$ in the droplet, defined as the percentage of the total reaction that takes place in the spherical slice between the surface and the distance x_i from the surface. Obviously $F(R_D)$ would represent the total reaction in the droplet, and it would be $F(R_D)=100\%$. Fig. 5 shows that around 50% of the total droplet reaction would take place in a surface layer of 1 nm thickness, to be compared with the droplet radius R_D = 1 μm = 1,000 nm.

A further effect that can increase the surface concentration of ionic species, both cations and anions in this case, is the interaction (co-adsorption) with some hydrophobic compounds that undergo surface accumulation [37, 47]. The accumulation of apolar compounds can modify some features of the air-water interface, including most notably the dielectric constant. The configuration water-organic layer-air can be more favourable to the occurrence of ionic species near the droplet surface compared to a water-air system [48]. Additionally, cations can interact with the delocalised π electrons of the aromatic rings and, if aromatic compounds are accumulated at the surface, the interface concentration of the cations would also be increased. The surface concentration of the anionic counter-ions would be increased as a consequence upon interaction with the cations. To date, experimental data of co-adsorption between aromatic molecules and inorganic species are only available for the case of benzene and nitrate salts [37].

The phenomenon of surface co-adsorption can be treated approximately by means of the Wagner-Onsager-Samaras (WOS) formalism. This is an adaptation to the treatment of interfaces of the Debye-Hückel theory of electrolyte [49]. In this simplified theory the ions are described as impenetrable charged spheres in a solvent that is treated as a continuous and structureless dielectric. The same features are retained in the WOS formalism, the main difference being that the Debye-Hückel theory adopts a spherical symmetry because the solution bulk is isotropic [48]. In contrast, the WOS formalism adopts a cylindrical symmetry to describe the interface.

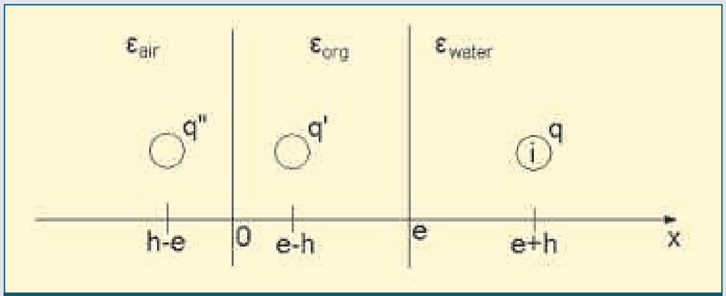

Fig. 7 - Schematic of an ion i (charge q) at distance h from the air-organic interface and of the image charges q' and q"

The Debye-Hückel theory considers the coulombic potential w_{ij} of the mean force acting between the ions i and j. Be i an ion of charge q at distance x from the interface. To take into account the anisotropy, the WOS treatment considers the potential w(x) of the force exerted on the ion i, with charge q, by the image charge q' located at a distance 2x from q (see Fig. 6).

In the presence of an organic compound that undergoes surface accumulation, it can be hypothesised that it forms a layer of thickness e and dielectric constant ε_{org} between water and air [50]. This is not unreasonable considering that the surface layer of atmospheric water droplets is more similar to an oily environment than to a simple air-water interface [51]. In such a case, for an ion of charge q at distance h from the water-organic interface one should consider the image charge q' inside the organic layer, and also the image q" of q' in the air phase (Fig. 7).

Fig. 8 shows the concentration profiles of benzene (bulk concentration 1 μM) and of nitrate (0.1 μM) as a function of the distance from the interface, in a droplet of 1 μm radius. For benzene it is hypothesised an accumulation of 400 times in a 0.5 nm layer near the interface. The nitrate profile is reported both in the absence of benzene, and in the presence of coadsorption of benzene and nitrate according to the WOS formalism [50].

The reported concentration profiles can have important consequence on photochemistry, considering that nitrate photolysis upon sunlight UV absorption yields $^{\bullet}$OH radicals (reaction 9) [52], which can react with benzene to give phenol with 95% yield [44]:

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}OH + {}^{\bullet}NO_2 \qquad (9)$$

As for H_2O_2, with 0.1 mM nitrate in a small droplet the rate of NO_3^- photolysis would be directly proportional to $[NO_3^-]$. Benzene would not be the main $^{\bullet}$OH scavenger in solution [45,46], thus it would be $r_{Phenol} \propto [Benzene][NO_3^-]$. In the absence of co-adsorption the reaction would be accelerated by the accumulation of benzene near the interface and, in a droplet of 1 μm radius, 5% of the total reaction

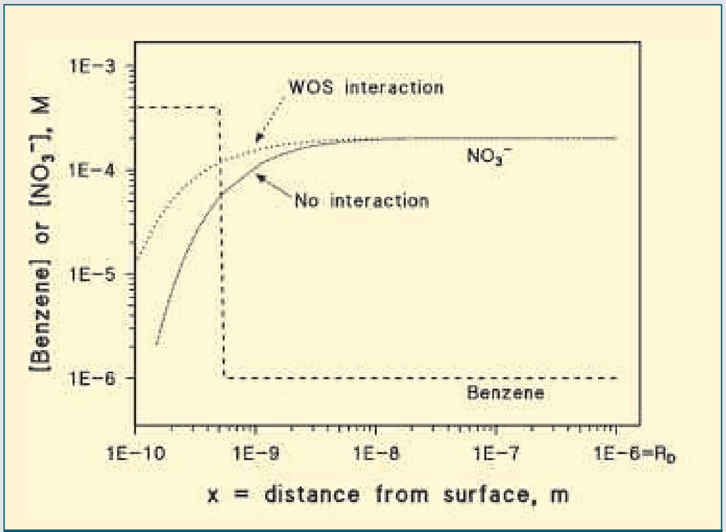

Fig. 8 - Concentration profiles of benzene and nitrate in a droplet of 1 μm radius (R_D). The profile of [NO_3^-] is reported both when it is alone, and upon the WOS interaction with benzene. It is evident that the co-adsorption enhances the concentration of nitrate near the interface

would take place in a surface layer of 1 nm thickness, accounting for just 0.3% of the total volume. If the co-adsorption of benzene and nitrate is considered, in the same surface layer it would take place around 15% of the total reaction of the droplet [50]. These data confirm the potential importance of the interfaces as efficient photoreactors in the atmosphere.

Solvent-cage effect on the photolysis quantum yields

Many compounds can be dissociated into fragments upon photon absorption. If the photolysis process occurs in the gas phase, the fragments would quickly diffuse away from each other and the probability of recombination would be very low. The situation is considerably different for a photolysis reaction that involves a molecule in the solution bulk. In this case the molecule is surrounded by the solvent and, following the primary bond breaking, photogenerated fragments would be formed in the same "solvent cage" that was surrounding the molecule before photolysis. In most cases the photogenerated "fragments" are radical species. Under these circumstances two competitive processes can take place. The first is the diffusion of the fragments out of the cage, in which case the radicals can react with dissolved molecules in the solution bulk. However, radical diffusion into the solution can be a relatively slow process due to the need of passing the barrier represented by the surrounding solvent molecules. The process of diffusion out of the cage is therefore in competition with the recombination of the fragments inside the cage to give the initial molecule. Recombination would decrease the photolysis quantum yield, when the latter is measured from the reactivity of the radical species that exit the cage [52]. Note that the radical-radical recombination out of the cage is usually very unlikely because of the low steady-state concentration values of the radical species in the solution bulk. This consideration is particularly relevant if one of the photogenerated radicals is $^{\bullet}OH$, which is efficiently scavenged out of the cage by dissolved organic matter and by many inorganic compounds [46].

In the case of the photolysis of H_2O_2 it has been found that the quantum yield in aqueous solution is around 0.5, much lower compared to the gas phase where it is near 1 [42, 43]. It has also been found that about 64-68% of photogenerated hydroxyl radicals can escape the solvent cage [53]. It would imply a photolysis quantum yield in the primary process (before recombination) of about 0.75, much nearer to that in the gas phase.

The solvent-cage effect on photolysis can be very relevant to the photochemistry of atmospheric droplets, and in particular to the photochemistry at the interface, because at the droplet surface the solvent cage is incomplete and the photogenerated fragments can avoid recombination. Accordingly, photolysis processes can be enhanced at the air-water interface of atmospheric droplets compared to the solution bulk [54, 55].

It has been found that the photodegradation of $Mo(CO)_6$ in 1-decene is increased by about 3 orders of magnitude in small liquid droplets (2 μm average diameter) compared to the bulk solution. The fast photodegradation in droplets has been explained with an increased photolysis quantum yield of $Mo(CO)_6$ at the air-water interface (incomplete solvent cage, see Fig. 9) [33].

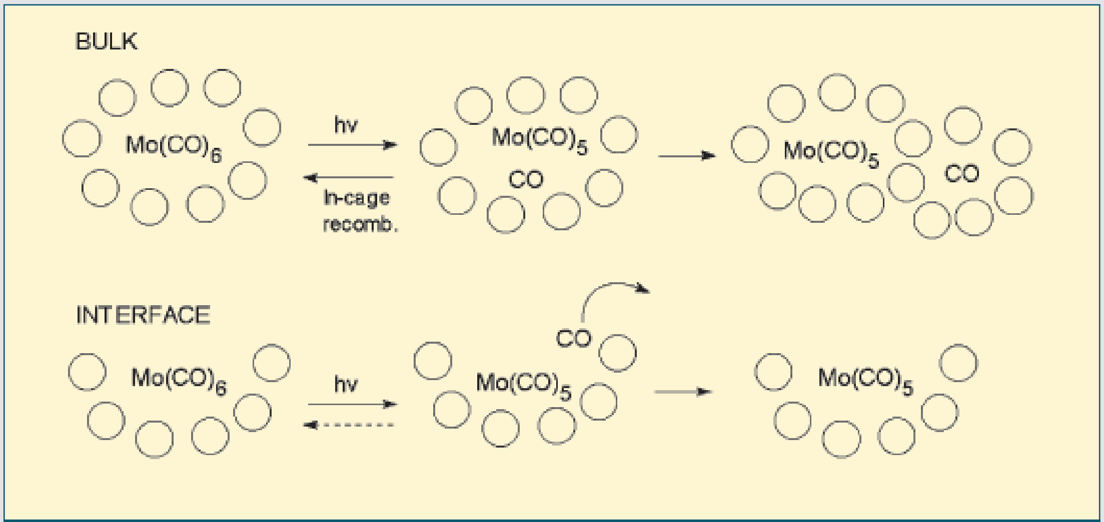

Fig. 9 - Schematic to explain the increased photodegradation kinetics of $Mo(CO)_6$ in small droplets, compared to the homogeneous solution

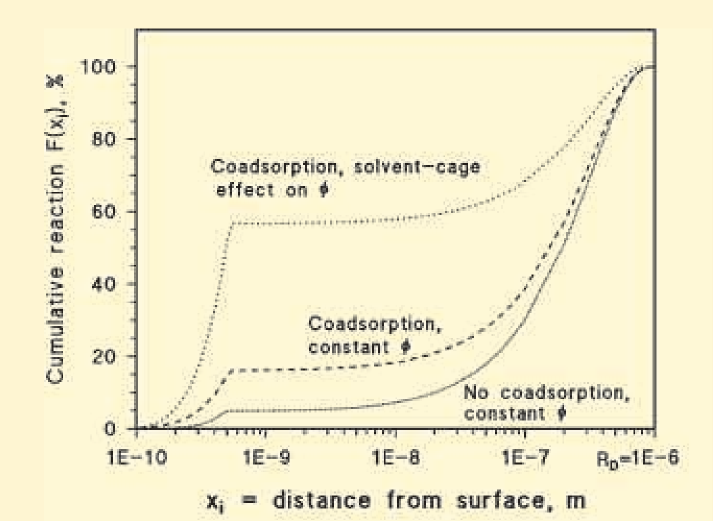

Fig. 10 -. Effects of the surface co-adsorption of benzene and nitrate and of the surface enhancement of the quantum yield of nitrate photolysis Φ_{NO3-} on the production of phenol from benzene. It was assumed a 6-fold enhancement of Φ_{NO3-} in a 0.5 nm surface layer

Solvent-cage effects have also been reported on the photolysis of nitrate (reaction 9), based on the observation that the photolysis reaction is enhanced upon addition of $^{\bullet}OH$ scavengers such as 2-propanol and bromide [56, 57].

Based on experimental results [46] it is possible to assume that, in the absence of the solvent-cage effect, the quantum yield of nitrate photolysis would be six times higher than in the solution bulk. The solvent cage is incomplete at the air-water interface of atmospheric droplets, where the described enhancement of the photolysis quantum yield might be observed. This effect would be added to the possible co-adsorption phenomena at the interface, such as the already described interaction between benzene and nitrate [50].

Fig. 10 considers a water droplet of 2 μm diameter (R_D=1 μm). It is apparent from the figure that, when all the surface effects are considered together, about 55% of the total droplet reaction would take place in a surface layer of around 1 nm thickness, which accounts for only 0.3% of the total droplet volume. This indicates the potential importance of the surface layer as an effective photochemical reactor. Additionally, the surface accumulation and co-adsorption phenomena would not modify to a significant extent the reaction rates in the solution bulk. The bulk reactions would therefore proceed at approximately the same rate that would be observed in the absence of interface phenomena. The surface reactions, which can be at least as important as the bulk ones, could therefore cause the reaction rates in the droplets to be double compared to a scenario in which the bulk processes only were operational.

Conclusions

Photochemical processes at the surface of atmospheric droplets could be very important because different phenomena are likely to increase the effectiveness of the interface as a photochemical reactor, compared to the solution bulk. First of all, irrespective of the interface effects, the droplet itself is a favourable environment for photochemistry due to increased irradiation intensity compared to the surrounding gas phase. The multiple reflections at the air-water interface would in fact increase the sunlight intensity in a drop by a factor η=1.3-1.8, depending on irradiation wavelength and droplet diameter.

From the Mie theory it is also derived that multiple reflections would not increase the irradiation intensity by the same extent in the whole droplet. On average, the irradiation intensity would be slightly lower (around 20%) at the droplet surface compared to the bulk [33].

Different phenomena could be able to enhance the rates of photochemical reactions at the interface, compared to the bulk of the droplet. First of all a number of photochemically active species in water droplets have a greater affinity for the interface [58], as is the case of O_3 and H_2O_2. The latter would undergo an accumulation factor of two at the droplet surface [38], where also some organic substrates are more concentrated than in the solution bulk [37]. The combination of increased concentration of both photoinducer (H_2O_2) and substrate (benzene) would make the photochemical reaction in a thin surface layer as important as that in the bulk, the latter accounting for over 99% of the droplet volume.

Inorganic ions that do not undergo surface accumulation themselves can be present at higher concentration at or near the interface due to the interaction with hydrophobic molecules that are accumulated at the surface, as in the case of nitrate and benzene [37]. The so-called co-adsorption phenomenon could give a significant contribution to the interface photochemistry [50].

Finally, at the air-water interface the solvent cage surrounding the photoactive molecules is incomplete. This could lead to a considerable enhancement of the photolysis processes at the interface, because the recombination of the photofragments would be less likely [52]. Nitrate photolysis could undergo a 6-fold enhancement at the interface due to the lack of solvent-cage inhibition [46]. The combined effects of co-adsorption and enhanced quantum yield of $^{\bullet}OH$ photogeneration at the interface could result into higher reactivity at the surface than in the bulk,

Davide Vione obtained the Ph.D. in Chemistry at the University of Torino in 2001. From November 2002 he has been University Lecturer in Analytical Chemistry at the Department of Analytical Chemistry of the University of Torino.

His research interests include the photochemical transformation of organic and inorganic compounds in surface and atmospheric waters, the study of advanced oxidation processes (heterogeneous photocatalysis, sonochemistry, Fenton systems) for water and wastewater decontamination, and the application of photocatalysis to the cosmetic field (sunscreen pigments).

where the vast majority of the droplet mass is concentrated.

Current models of atmospheric chemistry and photochemistry only take into account the bulk reactions in droplets [7, 59], and could therefore underestimate considerably the reactivity of atmospheric waters. It is thus very important to gain a more precise knowledge of the possible interface processes, their significance for a variety of chemical and photochemical reactions, and finally their impact on the reactivity of atmospheric droplets. The inclusion of such processes into the models of atmospheric reactivity would considerably increase the precision with which the models describe the real environment. The predictive capability of the models themselves would be increased as a consequence.

References

[1] R. Atkinson, *Pure Appl. Chem.,* 1998, **70,** 1327.
[2] D. Vione *et al., Chem. Soc. Rev.,* 2006, **35,** 441.
[3] C.A. Reyes *et al., Environ. Sci. Technol.,* 2000, **34,** 415.
[4] T.D.J. Dunstan *et al., Environ. Sci. Technol.,* 1989, **23,** 303.
[5] M. Jang, S.R. McDow, *Environ. Sci. Technol.,* 1995, **29,** 2654.
[6] M. Jang, S.R. McDow, *Environ. Sci. Technol.,* 1997, **31,** 1046.
[7] P. Warneck, *Phys. Chem. Chem. Phys.,* 1999, **1,** 5471.
[8] C. Anastasio *et al., J. Environ. Sci. Technol.,* 1997, **31,** 218.
[9] A. Feilberg, T. Nielsen, *Environ. Sci. Technol.,* 2001, **35,** 108.
[10] B.A. Southworth, B.M. Voelker, *Environ. Sci. Technol.,* 2003, **37,** 1130.
[11] M.N. Chan, C.K. Chan, *Environ. Sci. Technol.,* 2003, **37,** 5109.
[12] C, Anastasio *et al., Atmos. Environ.,* 2001, **35,** 1079.
[13] E. Bolzacchini *et al., Environ. Sci. Technol.,* 2001, **35,** 1791.
[14] D. Vione, *et al., Environ. Sci. Technol.,* 2005, **39,** 7921.
[15] C. Minero *et al., Environ. Sci. Pollut. Res.,* 2007, **14,** 241.
[16] D. Vione *et al., Environ. Sci. Technol.,* 2005, **39,** 5066.
[17] S. Chiron *et al., Environ. Sci. Technol.,* 2006, **40,** 5977.
[18] D. Vione *et al., ChemSusChem,* 2008, **1,** 197.
[19] T. Umschlag *et al., Phys. Chem. Chem. Phys.,* 2002, **4,** 2975.
[20] M.A. Harrison *et al., Atmos. Environ.,* 2005, **39,** 231.
[21] R.J. Atkinson, *Phys. Chem. Ref. Data,* 1994, monograph n° 2.
[22] G.V. Buxton *et al., J. Phys. Chem. Ref. Data,* 1988, **17,** 513.
[23] S.J. Madronich, *Geophys. Res.,* 1987, **92,** 9740.
[24] B. Mayer *et al., Geophys. Res. Lett.,* 1998, **25,** 4321.
[25] A. Ruggaber *et al., J. Atmos. Chem.,* 1994, **18,** 171.
[26] B. Mayer, S. Madronich, *Atmos. Chem. Phys.,* 2004, **4,** 2241.
[27] A. Ruggaber *et al., Atmos. Environ.,*1997, **31,** 3137.
[28] A. Bott, W. Zdunkowski, *J. Opt. Soc. Am. A,* 1987, **4,** 1361.
[29] M. Kerker, The scattering of light and other electromagnetic radiation, Academic Press: NY, 1969.
[30] C. Bohren, D. Huffman, Absorption and scattering of light by small particles, Wiley: NY, 1983.
[31] W. Wiscombe, *Appl. Opt.,* 1980, **19,** 1505.
[32] P.W. Barber, S.C. Hill, Light Scattering by Particles: Computational Methods, World Scientific, Singapore, 1990.
[33] P. Nissenson *et al., Phys. Chem. Chem. Phys.,* 2006, **8,** 4700.
[34] B. Minofar *et al., J. Phys. Chem. C,* 2007, **111,** 8242.
[35] B. Minofar *et al., J. Phys. Chem. B,* 2006, **110,** 15939.
[36] R. Vacha *et al., Phys. Chem. Chem. Phys.,* 2006, **8,** 4461.
[37] M. Sadiki *et al., Atmos. Environ.,* 2003, **37,** 3551.
[38] R. Vacha *et al., J. Phys. Chem. A,* 2004, **108,** 11573.
[39] P. Jungwirth, D.J. Tobias, *J. Phys. Chem. B,* 2002, **106,** 6361.
[40] O. Hofft *et al., J. Phys. Chem. B,* 2006, **110,** 11971.
[41] E.M. Knipping *et al., Science,* 2000, **288,** 301.
[42] D. Vione *et al., Ann. Chim. (Rome),* 2003, **93,** 477.
[43] B.J. Finlayson-Pitts, J.N. Pitts Jr., Atmospheric Chemistry, Wiley, NY, 1986.
[44] U. Deister *et al., Ber. Bunsenges. Phys. Chem.,* 1990, **94,** 594.
[45] A. Marinoni, *et al., Atmos. Chem. Phys.,* 2004, **4,** 715.
[46] C. Minero *et al., Chemosphere,* 2007, **68,** 2111.
[47] A. Acharid, *et al., Langmuir,* 2006, **22,** 8790.
[48] R.S. Berry *et al.,* J. Physical Chemistry, Wiley, NY, 1980.
[49] S. Onsager, N.N.T. Samaras, *J. Chem. Phys.,* 1934, **2,** 528.
[50] D. Vione *et al., Atmos. Environ.,* 2007, **41,** 3303.
[51] V.F. McNeill *et al., J. Phys. Chem. A,* 2007, **111,** 1073.
[52] J. Mack, J.R. Bolton, *J. Photochem. Photobiol. A: Chem.,* 1999, **128,** 1.
[53] R.A. Crowell *et al., Chem. Phys. Lett.,* 2004, **383,** 481.
[54] J.D. Graham *et al., J. Phys. Chem.,* 1996, **100,** 19551.
[55] A. Furlan, *J. Phys. Chem. B.,* 1999, **103,** 1550.
[56] P. Warneck, C. Wurzinger, *J. Phys. Chem.,* 1988, **92,** 6278.
[57] R.C. Bouillon, W.L. Miller, *Environ. Sci. Technol.,* 2005, **39,** 9471.
[58] P. Jungwirth, D. Tobias, *J. Chem. Rev.,* 2006, **106,** 1259.
[59] M.A.J. Harrison *et al., Atmos. Chem. Phys.,* 2005, **5,** 1679.

RIASSUNTO

Processi fotochimici superficiali nella fase acquosa atmosferica.

Le reazioni fotochimiche svolgono un ruolo importante nella trasformazione dei composti disciolti nelle acque atmosferiche (nubi, nebbie, foschie ecc.). In aggiunta, l'interfaccia aria-acqua è un interessante reattore fotochimico a causa di fenomeni di riflessione e rifrazione della radiazione all'interno delle gocce sferiche, dell'accumulo interfacciale di specie fotoattive e dell'incompletezza della gabbia del solvente che circonda le medesime specie.