Impact, Trapping, and Accommodation of Hydroxyl Radical and Ozone at Salt Aerosol Surfaces: A Molecular Dynamics Study

Martina Roeselová,[a*] Pavel Jungwirth,[a] Douglas J. Tobias,[b] and R. Benny Gerber[b,c]

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, and Center for Complex Molecular Systems and Biomolecules, Dolejškova 3, 18223 Prague, Czech Republic

[b] Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

[c] Department of Physical Chemistry and Fritz Haber Center for Molecular Dynamics, Hebrew University of Jerusalem, Jerusalem 91904, Israel

Version of March 14, 2003

*e-mail:roesel@jh-inst.cas.cz

Abstract

Collisions of the gaseous hydroxyl radical and ozone with surfaces of sodium chloride or iodide solutions as well as with the surface of neat water were investigated by molecular dynamics simulations. The principal aim was to answer atmospherically relevant questions concerning trapping and accommodation of the OH and O_3 species at the surface and their uptake into the bulk solution. Although trapping is substantial for both species, OH adsorbs and absorbs significantly better than O_3. While most of the trapped ozone molecules desorb from the surface within 50 ps, a significant fraction of hydroxyl radicals remains at the interface for time intervals exceeding 100 ps. The aqueous surface has also an orientational effect on the OH species, favoring geometries with the hydrogen pointing to the aqueous bulk. The effect of the dissolved salt on the trapping efficiency is minor, therefore, most likely, atomic ions solvated in aqueous aerosols do not act as scavengers of reactive gases in the atmosphere. There are, however, frequent and relatively long contacts between the adsorbed molecules and halide anions allowing for heterogenous atmospheric chemistry in the interfacial layer.

1 Introduction

Aerosols of different types have long been recognized to play major roles in a variety of processes of atmospheric importance [1, 2]. Processes on solid aerosols are generally considered to take place at the surface of the particle, while for liquid aerosols both homogeneous reactions and heterogeneous processes at the aerosol/air interface can be important, depending on the system [3–10]. Indeed, several atmospheric reactions of major interest have been attributed to heterogeneous chemistry taking place at the aerosol surfaces [3–6]. While qualitatively the evidence for the role of aerosols in atmospheric processes is strong, the microscopic mechanisms for the action of aerosols are poorly understood. To throw light on the detailed mechanisms whereby processes at aerosol surfaces take place, it is desirable to understand the uptake of the relevant molecules by the aerosol droplet, to describe the accommodation of the molecule at the surface once trapped, and to explore the dynamics of the reactions that eventually take place. Such a level of understanding was attained for a range of processes at the gas/surface interface, especially for single crystal surfaces. Rigorous, quantitative experiments using surface UHV techniques, combined with theoretical simulations at the atomic level of detail have often provided such insights [11–13]. Understanding of chemical dynamics at liquid/air surfaces is, on the whole, less advanced than for single crystal surfaces, but also for such systems major progress was made, often by the combination of microscopically sensitive experimental techniques with theoretical simulations from an atomistic point of view [14–18].

Our objective in this paper is to explore the dynamics of molecular interactions with liquid aerosol surfaces, using Molecular Dynamics (MD) simulations to describe the processes involved. Specifically, we shall explore the interaction of the atmospherically important species O_3 and OH with NaCl/water and related aqueous aerosols. There is strong evidence of efficient release of chlorine in heterogeneous reactions in these systems, at the surface of the aerosols [3]. In a previous paper, we explored the structure of the aerosols, and suggested that an enhanced presence of negative ions at the surface, may play a role in the mechanism [19]. In the present article, we investigate the uptake of molecules by the aerosol and study the accommodation dynamics and the behavior of the trapped species at the surface. These processes are of intrinsic interest, and it is hoped that understanding of these processes will ultimately throw light also on the chemical reactions and their mechanisms.

First, we addressed the question concerning the probability that a gas phase hydroxyl radical or an ozone molecule with a thermal velocity adsorbs at the interface. Second, we examined the probabilities that molecules initially adsorbed at the surface remain for a certain duration in the interface layer, become solvated in the bulk, or desorb back into the gas phase. Specifically, we wanted to know how much time on average does the adsorbed molecule spend on the surface before desorbing again or becoming fully solvated. Third, we tested the suggestion that halide ions exposed on the surface might act as scavengers that attract reactive species from the gas phase [19]. Finally, we investigated to what extend does the adsorbed hydroxyl radical get into direct contact with halide ions present in the interface layer. In particular, we wanted to assess, if the occurrence and duration of the contacts between OH and Cl^- are sufficient to support the surface mechanism of molecular chlorine production based on the formation of a $OH\ldots Cl^-$ complex [19].

The structure of the paper is as follows: Details concerning modeling of the system and the simulation approach are described in Sec. 2. Results are presented and discussed in Sec. 3. Conclusions are summarized in Sec. 4.

2 Systems and Computational Methods

Molecular dynamics simulations were carried out for a hydroxyl radical or an ozone molecule interacting with a water slab, either neat or containing sodium chloride at saturation (6.1 M) or sodium iodide at a concentration of 1.2 M. In the laboratory experiment, aimed at elucidating the reaction mechanism leading to production of molecular chlorine [19], the NaCl concentration in the aqueous salt aerosol particles was equal approximately to 4.5 M, while under atmospheric conditions, this concentration spans a broad interval, ranging from sea water concentrations to saturation. In addition, we studied aqueous sodium iodide at a concentration of 1.2 M, which is roughly the same as that employed in the experimental investigation of the uptake of ozone by aqueous solutions [44].

To construct the slabs, a rectangular cell of $30 \times 30 \times 100$ Å was used, containing 864 water molecules and 96 sodium and 96 chloride ions in the former case, or 18 sodium and 18 iodide ions in the latter. Application of such periodic boundary conditions at constant volume yielded an infinite slab with two open surfaces, perpendicular to the z-axis. For comparison, we carried out also simulations with a slab of neat water. In this case, 864 water molecules in an identical simulation cell were used.

The molecular dynamics simulations were performed using the AMBER 6 program package [20] with polarizable potentials [21–24]. Inclusion of atomic polarizabilities was shown to be crucial for the correct description of mixed halide anion–water clusters [23, 25] as well as aqueous salt solution/air interfaces [19, 26, 27]. The only difference between the force field reported in Refs. [19, 26, 27] and that employed in this work concerns the value of polarizability of the chloride ion. In the present simulations, we use a slightly higher value of 4.0 Å^3, which was suggested recently [28]. As far as the hydroxyl radical and ozone molecule are concerned, the geometrical parameters were taken from ab initio MP2/aug-cc-pvtz optimizations. The partial atomic charges were obtained at the MP2/6-31G level. All ab initio calculations were performed using the GAUSSIAN98 program package. [35]

For the atomic polarizabilities of oxygen and hydrogen atoms of the hydroxyl radical, values equal to those used for the water molecule were employed. The polarizability of the ozone molecule was obtained as a mean value of the diagonal elements of the polarizability tensor calculated at the MP2/aug-cc-pvtz level. One third of this value was then assigned to each of the three oxygen atoms of the ozone molecule. A test simulation, in which the whole polarizability of ozone was assigned entirely to the central oxygen, was carried out, and no substantial difference between the two models was observed. The force field parameters are summarized in Table 1. Check against ab initio calculations shows that this parameterization is satisfactory, but it slightly overestimates the Cl^-–H_2O binding and, at the same time, somewhat underestimates the OH–Cl^- binding. It is, apparently, difficult to accurately describe the OH radical–halide anion interaction by an empirical force field.

The adsorption of hydroxyl radical and ozone at the air/solution interface was investigated by running a series of scattering trajectories. First, an equilibrated configuration of the salt solution or neat water slab has been produced by a 0.5 ns MD trajectory. Using this slab configuration, 25 initial configurations for the scattering trajectories were generated by placing the hydroxyl radical or ozone molecule at random points in the xy-plane, 12.5 Å above the surface of the slab. In order to test, weather the initial orientation of the hydroxyl radical with respect to the surface might play a role in the simulations, two initial orientations of OH were considered, both with the O–H bond along the z-axis (i.e., perpendicular to the surface), one with oxygen facing the surface, the other with oxygen pointing away from the surface. Due to the orientational effect of the interface on hydroxyl radical (see Section 3), both sets of simulations provided statistically equivalent results for all slabs. In the case of ozone, only one initial orientation was taken into account, with the central oxygen atom pointing away from the surface and the two remaining oxygens placed symmetrically with respect to the z-axis and facing the surface. The initial velocity of the hydroxyl radical or ozone was set to the most probable value from the corresponding Maxwell-Boltzmann distribution at 300 K, and scattering under five different impact angles (0°, 22.5°, 45°, 67.5°, and 85°) was investigated. Using these initial conditions, a total number of 125 scattering trajectories, each of a 100 ps duration, were generated for OH and O_3 at the slab saturated with NaCl, at a neat water slab, and at a 1.2 M NaI/water slab. System geometries were monitored every picosecond. Trajectories, for which the hydroxyl radical or ozone spent less than 2 ps in the interfacial layer, were classified as a scattering event, while the rest of the trajectories were considered as adsorbtion. The classification was based on the Solvent Accessible Surface Area (SASA) technique. The accessible surface of the incoming OH or O_3 particle was evaluated using the Lee and Richards algorithm [30] with a probe radius of 1.2 Å. Depending on the SASA value, the configurations were sorted into three sets: 1) solute fully exposed (i.e., in the gas phase), 2) solute partially solvated (i.e., in interface), and 3) solute fully solvated (i.e., in the aqueous bulk).

A constant temperature of 300 K was maintained throughout the simulations. A time step of 1 fs was employed. All bond vibrations involving hydrogens were constrained using the SHAKE algorithm. Intermolecular interactions were truncated at 12 Å. A smooth particle mesh Ewald method was used to account for the long range electrostatic energies and forces [31].

3 Results and Discussion

The scattering simulations, described in detail in the previous section, start with a hydroxyl radical or an ozone molecule in the gas phase approaching the liquid/air interface with a thermal velocity. Upon hitting the surface, the molecule can either scatter back into the gas phase, or become adsorbed at the surface. Once adsorbed, the molecule can remain in the interface, desorb, or become solvated in the liquid bulk. A fully solvated molecule can remain in the bulk, or return back to the interface, across which it originally crossed into the bulk. Due to the slab geometry of the system with two interfaces, it can also diffuse towards the other interface and, eventually, desorb into the gas phase on the other side of the slab. As an illustration, three trajectories for hydroxyl radical interacting with a slab of a saturated NaCl solution are shown in Fig. 1. The first trajectory corresponds to direct scattering. The remaining two panels represent "sticking" trajectories, either with a later desorption back into the gas phase, or an uptake into the bulk.

3.1 Trapping probabilities

Out of 125 trajectories for hydroxyl radical (ozone) interacting with each of the three slabs, we found direct scattering for 18 (17) trajectories in the case of saturated sodium chloride solution/air interface, for 8 (17) trajectories in the case of neat water/air interface, and for 11 (5) trajectories in the case of 1.2 M sodium iodide solution/air interface. For all systems under study, the scattering/adsorption probability has been found to be almost independent of the incident angle, with direct scattering being slightly more probable for larger impact angles (grazing collisions). Fig. 2 shows three sets of trajectories for hydroxyl radical approaching different surfaces at the impact angle of 0° (i.e., perpendicularly to the surface). The upper panel corresponds to the saturated sodium chloride solution/air interface, the middle panel to the neat water/air interface, and the lower panel to the 1.2 M sodium iodide solution/air interface. Analogous sets of trajectories for ozone are presented in Fig. 3. For each trajectory, the z-coordinate of oxygen atom of the OH species, or of the central oxygen in the case of ozone, is plotted against time. For both OH and O_3, direct scattering occurs only for a small fraction of trajectories. For most of the trajectories these species are at least temporarily adsorbed at the surface and, in some cases (almost exclusively for OH), become later fully solvated. The trapping times of the solute, before desorbing back into the gas phase, span a large interval from few picoseconds to more than 100 ps, which is a technical limit given by the length of the simulations. Distributions of trapping times of hydroxyl radical for the three slabs are presented in Fig. 4, while analogous distributions for ozone are shown in Fig. 5.

A comparison between Figs. 2 and 3, as well as Figs. 4 and 5, clearly reveals a difference between the behavior of the hydroxyl radical and the ozone molecule. The basic message is that, on average, O_3 desorbs from the surface substantially faster than OH. Most of the ozone molecules leave the slab within 20 to 30 ps from the first contact with the surface, whereas a large fraction of the hydroxyl radicals remains adsorbed for the whole duration of the simulations. This difference in trapping behavior of hydroxyl radical and ozone molecule can be quantified by evaluating the mean trapping time $\bar{\tau}$ of the two species on the various surfaces. As can be seen from Table 2, for all three slabs the mean trapping times of O_3 are less than half of those of OH.

The integral trapping probability $P(t)$, i.e., the probability of surviving on the surface or in bulk of the slab for *at least* time t before desorbing back to the gas phase, was evaluated for all systems under study. The assessment of trapping was based on the SASA analysis (see Section I). The solute molecule was considered trapped as long as its solvent accessible surface area corresponded to partial or full solvation. If the solute became fully exposed in the gas phase for a period longer than 2 ps, it was considered desorbed. The results, for both OH and O_3, comparing the salt solutions to neat water, are presented in Fig. 6. For all three slabs, the ozone signals decay much faster than those of the hydroxyl radical, which corresponds to a more rapid ozone desorption from the surfaces. Somewhat surprisingly, the effect of the dissolved salt is rather small, especially in the case of ozone. For OH, the presence of iodide ions in the interface leads to a slight enhancement of trapping in the region of longer trapping times (t $>$ 50 ps). Desorption of OH from the saturated NaCl slab surface back into the gas phase is, however, somewhat faster than from the neat water surface.

The probability that a gas-phase molecule is accommodated on a liquid droplet is commonly expressed using the mass accommodation coefficient [38]. On the basis of scattering simulations, the mass accommodation coefficient α can be defined as follows [36]

$$\alpha = \frac{number\ of\ sticking\ trajectories}{total\ number\ of\ trajectories}. \tag{1}$$

In order to use this definition, one has to specify the minimal residence time τ_{res} of the adsorbate at the surface for a "sticking" trajectory. Mass accommodation coefficients for all systems under study are presented in Table 3 for four different minimal residence times (3, 10, 50, and 90 ps). We see that due to the desorption that occurs during the course of the simulations (see Figs 2, 3, and 6), increasing the minimal residence time τ_{res} reduces significantly the evaluated mass accommodation coefficients. Obviously, if the desorption back to the gas phase is not negligible, expression 1 does not provide a unique definition of mass accommodation coefficient in the realm of scattering MD simulations. As discussed in detail in Ref. [36], unlike the experimentally determined values that tend to represent a lower bound to the value of the mass accommodation coefficient, the present scattering MD simulations provide an upper bound. Consequently, only for longer minimal residence time the much stronger tendency of O_3 than OH to desorb from the surface reflects itself in the calculated mass accommodation coefficients. Also, evaluated numbers of sticking trajectories employing a longer minimal residence time ($\tau_{res} = 90ps$ for hydroxyl radical and $\tau_{res} = 50ps$ for ozone) lead to mass accommodation coefficients that approach (from above) the experimental values $\alpha(OH) = 0.1$ [41], and $\alpha(O_3) = 0.04$ [42] or $\alpha(O_3) > 0.02$ [43].

3.2 Absorption

Another profound difference between the behavior of hydroxyl radical and ozone concerns their propensity for bulk solvation. The probability that an ozone molecule, after having been adsorbed at the interface, becomes fully solvated in the bulk is very small for all slab systems. A trajectory has been classified as "absorption" if the solute has been fully solvated for longer than 5 ps. Only one such trajectory, with a 15 ps bulk solvation of O_3, was observed for the saturated NaCl solution slab, and two such trajectories (45 and 68 ps) for the 1.2 M NaI slab. No trajectory of this type has been found for ozone on a neat water slab.

Bulk solvation of the hydroxyl radical, however, has been observed for a substantially larger fraction of trajectories: 8 in the case of the saturated NaCl solution, 20 for neat water, and 33 for the 1.2 M NaI slab. The mean solvation times of OH in the two salt solutions are rather similar (28 ps in the saturated NaCl solution, 25.4 ps in the 1.2 M NaI solution) and somewhat longer than that in neat water (17.5 ps). Of the three slabs, the OH species solvates most easily in aqueous sodium iodide, i.e., the presence of iodide ions in the solution enhances the uptake of the hydroxyl radical into the bulk. This is different from the case of the sodium chloride solution, where a hydroxyl radical remains more confined to the interface region than in neat water. As a consequence, OH desorption back into gas phase is faster from a NaCl solution than from a neat water. However, one should have in mind that this effect might be partly due to inaccuracies in the present force field (slightly overestimated H_2O–Cl^- and underestimated OH–Cl^- interactions, as discussed in Section 2).

3.3 Density profiles

A useful way of visualizing the occurrence of the solutes at the surface or in the bulk as well as the typical depth of penetration of the solutes into the slabs is to calculate density profiles along the direction perpendicular to the surface of the slab (z-axis). For slab simulations, it is usual to average the density profiles over the two roughly equivalent halves of the slab. In Figs. 7 and 8 we show the density profiles of hydroxyl radical and ozone, together with those for the water oxygens, for the three investigated slabs. The interval on the z-axis in which the water oxygen signal drops from the plateau corresponding to the bulk water density to zero correlates with the interfacial region. However, due to the large corrugation of the surface as well as due to the presence of the ions in the interface of the salt solution systems, this quantity is only orientational. Depending on the salt concentration, the position of the interfacial layer and its thickness differ a little for each slab. Nevertheless, we see that surface adsorption dominates in all systems. The signal from the solutes adsorbed at the surface of the salty slabs (especially in the case of the saturated NaCl solution) is shifted slightly more outwards compared to neat water. This can be rationalized in terms of the contact with the halide ions in the interfacial layer (see below).

Comparing Fig. 7 and Fig. 8 we see that the signal of ozone in the gas phase region is about twice that of the hydroxyl radical. This fact is in agreement with the observation that the desorption of ozone back into the gas phase is faster than that of the hydroxyl radical. The signal from ozone in the aqueous bulk is close to zero for all slabs, which indicates very little absorption. Still, an enhancement of ozone uptake into the bulk of the 1.2 M NaI solution roughly by a factor of two compared to neat water can be seen from the bottom panel of Fig. 8. OH also prefers interfacial over bulk solvation. However, this dipolar species solvates in water and aqueous solutions substantially better than the almost non-polar ozone molecule. The OH signal in the interior of the slabs is at least one order of magnitude (in the case of the saturated NaCl solution even three orders of magnitude) larger than that of O_3. Finally, a comparison of the three panels of Fig. 7 shows that the propensity of OH for the interface is larger in the saturated NaCl solution than in neat water, while the opposite is true for the in 1.2 M NaI solution.

In order to quantify the above findings, we used the output of the SASA analysis and calculated the total number of interfacial and bulk configurations (for exact definitions see Section 1). The resulting numbers, summarized in Table 4, represent the total time in picoseconds of all trajectories the solute spent in the interface or in bulk, before desorbing back into the gas phase. The numbers presented in Table 4 are based on the analysis of each individual configuration saved during all simulations, without being possibly biased by assumptions concerning previous definitions of "scattering", "trapping", or "absorption". In this sense, Table 4 contains information which is independent of the trajectory-based quantities discussed earlier. Nevertheless, this complementary approach leads to conclusions that are fully consistent with the results presented above. The total time the solute was trapped by a given slab (either at the interface or in the bulk) is about twice as long for OH than for O_3. This also correlates very well with the calculated mean trapping times (see Table 2). A somewhat faster desorption of the hydroxyl radical from the saturated NaCl solution surface compared to the other two slabs manifests itself in the smaller number of "trapped" configurations in this case. The large difference between the two solutes (at least of one order of magnitude) in the total time spent in the bulk is in accord with the poor aqueous solubility of ozone compared to hydroxyl radical. The trapping of ozone at the surface is almost the same for all three slabs, however, the uptake of ozone into the bulk is enhanced by more than one order of magnitude by the presence of iodide ions in the solution compared to neat water, in agreement with the results of recent experimental studies [43, 44]. The enhancement of bulk solvation in the NaI solution is pronounced also in the case of OH.

3.4 Orientational effects

In the interfacial region, there is a strong preference for the hydroxyl radical to be parallel to the surface or to be oriented perpendicularly to the surface with the hydrogen atom pointing towards the slab. This orientational effect of the interface on the hydroxyl radical is clearly visible in all of the three trajectories depicted in Fig. 1. In an attempt to demonstrate this effect in a more quantitative way, we plotted in Fig. 9 the orientational distribution $P(cos(\theta))$ of the O→H bond vector with respect to the surface normal (see Fig. 9). The upper panel of Fig. 9 corresponds to the saturated NaCl solution slab, the middle panel to the neat water slab, and the lower panel to the 1.2 M NaI solution slab. The orientational probability distributions for the gas phase, for the interface, and for the bulk was obtained by averaging separately over each of the corresponding set of configurations, as defined in Section I.

As expected, the orientation of the hydroxyl radical in the gas phase as well as in the bulk is entirely random and is, therefore, described by a uniform probability distribution. However, all the probability distributions describing the interfacial configurations exhibit a pronounced minimum for $\cos(\theta) = 1$ (θ being the angle between the O→H bond vector and the surface normal). Thus, in the interface, the oxygen atom of the hydroxyl radical tends to point away from the slab. In the neat water case, the probability distribution for the interface peaks close to $\cos(\theta) = -1$, which corresponds to the O–H bond being perpendicular to the surface with the hydrogen atom facing towards the bulk. The analogous distributions for the two salt solutions exhibit a plateau region between $\cos(\theta) = -1$ and $\cos(\theta) = 0$, suggesting that there is an almost equal probability for any orientation of the hydroxyl radical between the O–H bond being perpendicular to the surface (with hydrogen facing the slab) and the O–H bond being parallel with the surface. The observed behavior of OH is clearly connected with the orientation of water molecules themselves in the interfacial layer [27, 37].

3.5 Surface solvation and contact of OH with halide ions

We used the simulations to gain a microscopic insight into the (partial) solvation of the two species under study in the interfacial region. First, we evaluated for each case the solute–halide, solute–sodium, and solute–water oxygen radial distribution functions (RDF) taking into account all configurations when the solute was situated in the interface. The RDFs were calculated from the geometrical center of the solute, i.e. from the center of the O–H bond or, in the case of ozone, from the center of the O_1–O_2–O_3 triangle. In Fig. 10, the resulting curves for hydroxyl radical adsorbed at the surface of both saturated NaCl solution and 1.2 M NaI solution are presented. For both solutions, the peaks corresponding to the halide ions and water oxygens in the first solvation shell around the hydroxyl radical are well pronounced. The sodium ions are almost absent from the interfacial layer, which results in the suppression of the first peak on the OH–Na RDFs. Analogical RDF curves for ozone are shown in Fig. 11. Due to the fact that ozone molecules spend much less time at the interface than OH, curves in Fig. 11 have poorer statistics compared to those in Fig. 10. Nevertheless, the peaks corresponding to the nearest water molecules, and in the case of the saturated NaCl slab, also to the nearest chloride ions are well pronounced. In the case of the 1.2 M NaI slab, the poor iodide statistics leads to a noisy RDF signal on which the first peak around 5 Å, but not the first subsequent minimum can be identified.

To address the question of the contact between the hydroxyl radical and the halide ions that are present in the surface layer of the salt solution, we analyzed all configurations recorded in the course of the simulations, for which the hydroxyl radical was located in the interface. For each configuration, we calculated the number of water molecules and halide ions in the first solvation shell of hydroxyl radical, i.e., the number of particles the distance of which from the center of the O–H bond fell below a certain threshold. The critical values were set to 5.1 Å for OH–Cl^-, 5.5 Å for OH–I^-, and to 5.0 Å for OH–water oxygen, which correspond to minima after the first peaks of the corresponding RDFs (see Fig. 10). By averaging over all surface configurations, we evaluated the average number of nearest neighbors of the hydroxyl radical located in the interfacial layer. The results (see Table 5) indicate, that an OH radical, trapped at the surface of the salt solution, is on average surrounded by slightly less than six water molecules. In addition to waters, it is about 60 per cent of the time in a direct contact with a chloride ion (in the saturated NaCl slab), or around 30 per cent of the time in contact with iodide ion (in the 1.2 M NaI slab). A simultaneous contact with more than one halide ion occurred in a negligible number of configurations.

We have also recorded the length of each contact between the hydroxyl radical and a halide ion. Distribution of the contact times t_{cont} is presented in Fig. 12. In most of the cases, the OH–X^- contact lasted between 1 and 5 ps. The average contact time was 2.9 ps for OH–Cl^-, and 2.25 ps for OH–I^-. However, in some cases the OH–X^- contact was substantially prolonged. About 20 % of the OH–Cl^- contact events were longer than 5 ps, and 3 % even longer than 10 ps. The maximum duration of the contact reached almost 20 ps. As far as the OH–I^- contacts are concerned, 10 % were longer than 5 ps and 1 % longer than 10 ps, with a maximum somewhat below 15 ps.

Contacts between OH and Cl^- are also seen in a series of snapshots from a typical "sticking" trajectory of OH at the saturated NaCl solution surface (the same trajectory as in Fig. 1b), shown in Fig. 13. In this particular trajectory, the OH initially "landed" on a part of the surface covered by water molecules. Within six picoseconds it migrated to a chloride ion, in the vicinity of which it stayed for the next ten picoseconds. Then, around t=20 ps, the hydroxyl radical raised slightly above the interface and jumped over to another part of the surface. There, subsequent contacts with three different chloride ions occurred (for 3, 1, and 4 ps, respectively) before OH desorption back into the gas phase. The last panel in Fig. 13 shows the whole trajectory of the hydroxyl radical on the surface (in the xy-plane). This figure demonstrates the mobility of the hydroxyl radical trapped at the surface of the aqueous salt solution, as well as the rather high probability of its contact with chloride ions present in the interface. We see an essentially diffusive motion of OH in the interface with chloride anions serving as weak attractors.

4 Conclusions

We have investigated, using molecular dynamics simulations, collisions of OH and O_3 with the surface of neat water and that of NaCl or NaI solution. For both gaseous species, we have found substantial trapping. On average, OH stays much longer at the interface and has also a higher probability to solvate into the bulk than ozone. Also, at the interface, OH becomes oriented with hydrogen rarely pointing away from the aqueous bulk. Somewhat surprisingly to us, the effect of the dissolved salt on the trapping of OH or O_3 is very small. Most probably, solvated halide ions do not particularly help in scavenging gases from the atmosphere into aqueous aerosols. It follows from the present simulations that there are, however, frequent and sufficiently long contacts between OH and Cl^- to make the suggested surface mechanism of photochemical production of molecular chlorine from aqueous sea-salt aerosols plausible [19].

Acknowledgement

The authors thank Barbara Finlayson-Pitts for valuable comments. Support from the NSF via a grant No. CHE-0209719 is gratefully acknowledged. Work at the Hebrew University was supported by the Israel Science Foundation (ISF grant No. 127/00-3 to RBG). The Center for Complex Molecular Systems and Biomolecules is supported by the Czech Ministry of Education (grant No. LN00A032).

References

[1] Wayne, R. P. in *Chemistry of Atmospheres*, Oxford University, Oxford, 2000.

[2] Finlayson-Pitts, B. J.; Pitts, J. N. in *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, 2000.

[3] Oum, K. W.; Lakin, M. J.; DeHaan, D. O.; Brauers, T.; Finlayson-Pitts, B. J. *Science* **1998**, *279*, 74.

[4] Vogt, R.; Crutzen, P. J.; Sander, R. *Nature* **1996**, *383*, 327.

[5] Finlayson-Pitts, B. J.; Ezell, M. J.; Pitts, J. N., Jr. *Nature (London)* **1989**, *337*, 241.

[6] Andreae, M. O.; Crutzen, P. J. *Science* **1997**, *221*, 744.

[7] Levy, D. J.; Lee, A. M.; Toumi, R.; Newchurch, M. J.; Pirre, M.; Renard, J. B. *J. Geophys. Res.* **1997**, *102*, 3671.

[8] Chameidas, W. L.; Davis, D. D. *J. Geophys. Res.* **1982**, *87*, 4863.

[9] Hendrick, J.; Lippert, E.; Petry, H.; Ebel, A. J. *J. Geophys. Res.* **1999** *104*, 5531.

[10] Ellison, G. B.; Tuck, A. F.; Vaida, V. *J. Geophys. Res.* **1999** *104*, 11633.

[11] Barker, J. A.; Auerbach, D. J. *Surf. Sci. Rep.* **1984**, *4*, 1.

[12] Gerber, R. B. *Chem. Rev.* **1987**, *87*, 29.

[13] Rettner, C. T.; Auerbach, D. J.; Tully, J. C.; Kleyn, A. W. *J. Phys. Chem.* **1996**, *100*, 31.

[14] Nathanson, G. M.; Davidovits, P.; Wornsop, D. R.; Kolb, C. E. *J. Phys. Chem.* **1996**, *100*, 31.

[15] Saecker, M. E.; Govoni, S. T.; Kowalski, D.; King, H. E.; Nathanson, G. M. *Science* **1991**, *252*, 1421.

[16] Saecker, M. E.; Nathanson, G. M. *J. Chem. Phys.* **1994**, *100*, 3999.

[17] Lipkin, N.; Gerber, R. B.; Moiseyev, N.; Nathanson, G. *J. Chem. Phys.* **1994**, *100*, 8408.

[18] Benjamin, I.; Wilson, M. A.; Pohorile, A.; Nathanson, G. M. *Chem. Phys. Lett.* **1995**, *243*, 222.

[19] Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabbub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.

[20] Case, D. A.; Pearlman, D. A.; Caldwell, J. W.; Cheatham III, T. E.; Ross, W. S.; Simmerling, C. L.; Darden, T. A.; Merz, K. M.; Stanton, R. V.; Cheng, A. L.; Vincent, J. J.; Crowley, M.; Tsui, V.; Radmer, R. J.; Duan, Y.; Pitera, J.; Massova, I.; Seibel, G. L.; Singh, U. C. AMBER6, University of California, San Francisco, 1999.

[21] Caldwell, J.; Dang, L. X.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 9144.

[22] Perera, L.; Berkowitz, M.J. *J. Chem. Phys.* **1991**, *95*, 1954.

[23] Perera, L.; Berkowitz, M.J. *J. Chem. Phys.* **1994**, *100*, 3085.

[24] Markovich, G.; Perera, L.; Berkowitz, M.J.; Cheshnovsky, O. *J. Chem. Phys.* **1996**, *105*, 2675.

[25] Tobias, D. J.; Jungwirth, P.; Parrinello, M. *J. Chem. Phys.* **2001**, *114*, 7036.

[26] Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2000**, *104*, 7702.

[27] Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105*, 10468.

[28] Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2002**, *106*, 6361.

[29] Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *23*, 327.

[30] Lee, B.; Richards, F. M. *J. Mol. Biol.* **1971**, *55*, 379.

[31] Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Pedersen, L. G. *J. Chem. Phys* **1995**, *103*, 8577.

[32] Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

[33] Kendall, R. A.; Dunning, Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

[34] Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

[35] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B. *et al.* GAUSSIAN98, Gaussian, Inc., Pittsburgh PA, 1998.

[36] Wilson, M. A.; Pohorille, A. *J. Phys. Chem. B* **1997**, *101*, 3130.

[37] Taylor, R. S.; Dang, L. X.; Garrett, B. C. *J. Phys. Chem.* **1996**, *100*, 11720.

[38] Taylor, R. S.; Ray, D.; Garrett, B. C. *J. Phys. Chem. B* **1997**, *101*, 5473.

[39] Taylor, R. S.; Garrett, B. C. *J. Phys. Chem. B* **1999**, *103*, 844.

[40] Hamad, S.; Lago, S.; Mejias, J. A. *J. Phys. Chem. A* **2002**, *106*, 9104.

[41] Frost G.J., Trainer M., Mauldin R.L., Eisele F.L., Prevot A.S.H., Flocke S.J., Madronich S., Kok G., Schillawski R.D., Baumgardner D., Bradshaw J. *J. Geophys. Res.-Atmos.* **1999**, *104*, 16041.

[42] Muller B., Heal M.R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3365.

[43] Schutze M., Herrmann H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 60.

[44] Magi, L.; Schweitzer, F.; Pallares, C.; Cherif, S.; Mirabel, P.; George, C. *J. Phys. Chem. A* **1997**, *101*, 4943.

Figure Captions

Fig. 1 Example of three types of trajectories in scattering simulations: (a) direct scattering, (b) adsorption with subsequent desorption, (c) adsorption with subsequent uptake into the bulk liquid.

Fig. 2 Three sets of trajectories (25 trajectories each) for OH approaching different surfaces at the impact angle of 0° (i.e., perpendicularly to the surface). Scattering from (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution. For each trajectory, the z-coordinate of the oxygen atom of the hydroxyl radical is plotted against time. The dashed lines define the interfacial layer.

Fig. 3 Three sets of trajectories (25 trajectories each) for O_3 approaching different surfaces at the impact angle of 0° (i.e., perpendicularly to the surface). Scattering from (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution. For each trajectory, the z-coordinate of the central oxygen atom of ozone is plotted against time. The dashed lines define the interfacial layer.

Fig. 4 Distribution of trapping times of OH at or in (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution.

Fig. 5 Distribution of trapping times of O_3 at or in (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution.

Fig. 6 Comparison of integral trapping probabilities of OH and O_3 for the salt solution slabs (full lines) and the neat water slab (dashed lines): (a) OH and the saturated NaCl solution, (b) O_3 and the saturated NaCl solution, (c) OH and the 1.2 M NaI solution, and (d) O_3 and the 1.2 M NaI solution.

Fig. 7 Density profiles of OH at (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution. Dashed lines denote the density profiles of water oxygens.

Fig. 8 Density profiles of O_3 at (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution. Dashed lines denote the density profiles of water oxygens.

Fig. 9 Orientational distributions of the O$\rightarrow$H vector relative to the surface normal for (a) the saturated NaCl solution, (b) neat water, and (c) the 1.2 M NaI solution. Dashed lines: orientation of OH in the gas phase above the surface, solid lines: orientation of OH in the interfacial layer, and dash-dotted lines: orientation of OH in the bulk liquid. $\cos(\theta) = 1$ corresponds to the O$\rightarrow$H vector parallel to the surface normal with the hydrogen atom pointing away from the interface, $\cos(\theta) = 0$ corresponds to the O$\rightarrow$H vector being perpendicular to the surface normal, and $\cos(\theta) = -1$ corresponds to the hydrogen atom facing the surface.

Fig. 10 Radial distribution functions for OH adsorbed at the interface of (a) the saturated NaCl solution, and (b) the 1.2 M NaI solution. Solid line corresponds to OH–X^- RDF (X=Cl, I), dashed line corresponds to OH–Na^+ RDF, and dotted line corresponds to OH–water oxygen RDF. The RDFs have been evaluated from the center of the O–H bond.

Fig. 11 Radial distribution functions for O_3 adsorbed at the interface of (a) the saturated NaCl solution, and (b) the 1.2 M NaI solution. Solid line corresponds to O_3–X^- RDF (X=Cl, I), dashed line corresponds to O_3–Na^+ RDF, and dotted line corresponds to O_3–water oxygen RDF. The RDFs have been evaluated from the center of the O_1–O_2–O_3 triangle.

Fig. 12 Distribution of contact times of OH with (a) chloride ions in the interface of the saturated NaCl solution, and (b) iodide ions in the interface of the 1.2 M NaI solution.

Fig. 13 (a-e) Series of snapshots from a typical "sticking" trajectory showing hydroxyl radical adsorbed at the surface of the saturated NaCl solution. Color coding: grey = hydrogen, blue = OH oxygen, red = water oxygen, yellow = Cl^-, green = Na^+. (f) The whole trajectory projected into the xy-plane. Yellow circles indicate contacts of OH with Cl^-.

Table 1: Force field parameters

	q [e]	α [Å^3]	σ [Å]	ϵ [kcal/mol]
Na^+	1.0	0.24	1.532	0.100
Cl^-	-1.0	4.00	2.509	0.118
I^-	-1.0	6.90	2.890	0.100
H_2O:				
O	-0.73	0.528	1.798	0.156
H	0.365	0.170	0	0
OH:				
O	-0.4	0.528	1.798	0.156
H	0.4	0.170	1.32	0.022
O_3:				
O_{center}	-0.06	0.770	1.798	0.156
O_{side}	0.11	0.770	1.798	0.156

Table 2: Mean trapping times

	$\bar{\tau}$ [ps]
OH @ NaCl slab	43.0
OH @ water slab	50.4
OH @ NaI slab	53.0
O_3 @ NaCl slab	16.2
O_3 @ water slab	18.1
O_3 @ NaI slab	22.0

Table 3: Mass accommodation coefficients α calculated for several values of minimal residence time τ_{res}

τ_{res} [ps]	3	10	50	90
OH @ NaCl slab	0.86	0.75	0.42	0.20
OH @ water slab	0.94	0.84	0.46	0.26
OH @ NaI slab	0.91	0.86	0.47	0.31
O_3 @ NaCl slab	0.88	0.54	0.06	0.016
O_3 @ water slab	0.87	0.74	0.08	0.008
O_3 @ NaI slab	0.96	0.70	0.11	0.016

Table 4: Total time (in ps) spent in interface / in bulk

	interface	bulk
OH @ NaCl slab	5199	317
OH @ water slab	6044	783
OH @ NaI slab	5509	1400
O_3 @ NaCl slab	2784	12
O_3 @ water slab	2887	4
O_3 @ NaI slab	2857	115

Table 5: Average number of halide ions (X = Cl, I) and water molecules in the first solvation shell of OH in interface

	X^-	H_2O
OH @ NaCl slab	0.61	5.70
OH @ NaI slab	0.28	6.41