

Question List for Dr. Joseph Francisco

Carleton College Chemistry Department

Senior Integrative Exercise

May 4-5, 2023

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Papers We Read in Detail

71. Kumar, M.; Trabelsi, T.; Martín, J. C. G.; Saiz-Lopez, A.; Francisco, J. S. HIOx-IONO2 Dynamics at the Air-Water Interface: Revealing the Existence of a Halogen Bond at the Atmospheric Aerosol Surface. *J. Am. Chem. Soc.* **2020**, *138*, 12467-12477. <https://doi.org/10.1021/jacs.0c05232>

137. Ge, C.; Zhu, C.; Francisco, J. S.; Zeng, X. C.; Wang, J. A Molecular Perspective for Global Modeling of Upper Atmospheric NH₃ from Freezing Clouds. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 6147-6152. <https://doi.org/10.1073/pnas.1719949115>.

162. Kumar, M.; Francisco, J. S. Ion Pair Particles at the Air-Water Interface. *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 12401-12406. <https://doi.org/10.1073/pnas.1709118114>.

207. Zhu, C.; Kumar, M.; Zhong, J.; Li, L.; Francisco, J. S.; Zeng, X. C. New Mechanistic Pathways for Criegee-Water Chemistry at the Air/Water Interface. *J. Am. Chem. Soc.* **2016**, *138*, 11164-11169. <https://doi.org/10.1021/jacs.6b04338>.

261. Anglada, J. M.; Martins-Costa, M.; Ruiz-López, M. F.; Francisco, J. S. Spectroscopic Signatures of Ozone at the Air-Water Interface and Photochemistry Implications. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 11618-11623. <https://doi.org/10.1073/pnas.1411727111>.

General questions

General Big Picture Questions

1. **LUCY:** How did you get started in this type of research? What drew you to studying atmospheric chemistry and particularly the air-water interface? What did research in chemistry at the air-water interface look like at the time you started your work and how has it evolved over time?
2. **ANIA:** What are your thoughts on geoengineering climate change solutions like cloud seeding? What about sulfate aerosols?
3. **NELL:** The most pressing issues that a person not involved in atmospheric science most likely knows of is climate change and the depletion of ozone over Antarctica. As an atmospheric chemist, what do you believe are the biggest issues and unsolved questions in the field today?

Research Process

4. **SEAN:** What is the general structure of your lab? How many projects is your lab working on at a single time and how many are you directly involved in? How do you approach a collaboration between research groups? How many of your collaborations involve working together on the motivations of the study, and how many are closer to doing a requested computation for someone else's project?
5. **WILL:** How do you decide when to do a series of studies on a particular system versus moving to other systems? What is your process for choosing topics in general?
6. **EMMA:** What are some of the ways you think about whether to put a figure referenced in the text into the paper or the supporting information?

Research Details

7. **WILLIAM:** Can you ever argue that a process doesn't happen? Similarly, how do you consider kinetics and whether a process is just slow or can be considered to "not happen?" How do you balance the kinetic data (rates and molecular dynamics timesteps) with thermodynamic data (equilibria, gas-phase binding energies)? Do you try to include both to some degree or is one generally more applicable to your work?
8. **NORA:** What kind of considerations go into deciding how many simulations to run for a given project? Is there a specific number that is deemed accurate for depicting a given chemical system, or does it depend specifically on the system in question?
9. **LUCY:** How do you approach studying systems where there are many R group derivatives (R_2COO , R_2NH , etc.) that all have a slightly different reactivity? You obviously can't do computational work for every single molecule, so what goes into the thinking about extrapolating these conclusions to other derivatives? How do you choose a set of R groups to study that make it maximally representative?

Air-Water Interface

10. **ANIA:** In many of your papers that we looked at, you defined the air water interface as a certain distance range (\AA), often based on the observed distance the molecule of interest traveled when placed at or above the air water interface in a simulation (ex. **Figure 1** and **S1** from *Spectroscopic Signatures of Ozone at the Air–Water Interface and Photochemistry Implications*). Is defining the extent of the air water interface for a system always based on the range of where the molecules stay during the simulations or are there any standards for minimum/maximums for this range? Do you ever encounter a circular argument for defining the extent of the air-water interface as where the molecules are during the majority of the simulation and using that to explain the interfacial preference of the molecules?

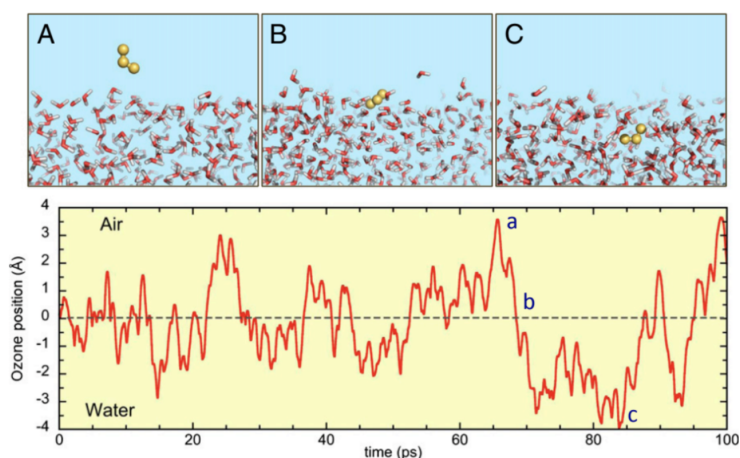


Fig. 1. Results from the 100-ps QM/MM molecular dynamics simulation. Upper snapshots (A–C) illustrate three characteristic situations of ozone (yellow) at the air–water interface with very different solvation patterns (from gas phase-like to bulk solution-like). (Lower) Time fluctuations of ozone center of mass with respect to the average air–water interface.

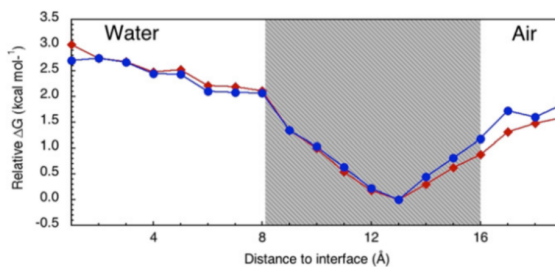


Fig. S1. Calculated free energy profiles using the dual level QM/MM method. The low-level calculations (HF/STO-3G, red diamonds) are carried out for sampling. Free energy perturbation corrections are carried out to obtain the relative free energy at a higher level [B3LYP/6-311+G(d), blue circles].

11. **NELL:** Mostly, your papers that we looked at were looking at chemistry occurring at the air-water interface in the atmosphere (i.e. clouds) but is the interface at the oceans comparable in contributions? Or does the complexity of marine environments make it difficult to compare the results from cloud air-water interfaces to oceanic air-water interfaces? Additionally, are the insights from the air-water interface in the atmosphere transferable to any other ideas - mineral surfaces, weathering, dust, etc.? What about non-aqueous aerosols? What about non-atmospheric

or non-environmental systems, for example, liquid-liquid interfaces or liquid-solid interfaces in batteries?

Computational methods

12. **SEAN:** Although the computational methods of your work were not our focus, we were curious about some aspects of the computation details. For one, many of your earlier works focus on single geometry energies and vibrational frequencies, and many of the more recent works feature MD simulations at the forefront of the project. How has this focus or research process shifted over the course of your career? How do you foresee it continuing to change as you continue research projects? Is your current research looking at any new MD methods? How have the computational methods that you've employed changed throughout your career? Where do you think the future of computational methods is going? What are the possibilities for time-dependent DFT?
13. **WILL:** Several of your papers choose to model the air-water interface as either a water droplet (*Ion Pair Particles at the Air-Water Interface* and *A Molecular Perspective for Global Modeling of Upper Atmospheric NH₃ from Freezing Clouds.*) or a wrapped cube with a completely planar surface on the top and bottom (*Spectroscopic Signatures of Ozone at the Air-Water Interface and Photochemistry Implications*). What goes into deciding to model the water part of the air-water system as a droplet or as a cube? The air-water interface of a water droplet in the atmosphere is a sphere, not a cube, so in that way a spherical water droplet with its entire surface as the air-water interface would be the most accurate. But as the radius of the droplet increases, the surface approaches what could be modeled well as a planar surface. Is there a computational advantage to modeling the interface one way or the other? Does the particular curvature of a water droplet play a role in reactivity? It seems like this could also depend on the size of the molecules involved in reactivity, because larger molecules would “feel” the curved surface more. Is this a consideration when determining how to model the surface?
14. **WILLIAM:** When do you use MD snapshots to find an approximate transition-state (TS) (*Ion Pair Particles at the Air–Water Interface*) versus deciding to calculate an exact transition-state from a saddle point on the PES (*New Mechanistic Pathways for Criegee-Water Chemistry at the Air/Water Interface*)? When identifying a transition state structure from MD, how do you decide what the most TS-like point is? When calculating an exact TS, do you always use the same approach to finding it? How have those methodologies changed over time?
15. **NORA:** As we saw in our reading of *Revealing the Existence of a Halogen Bond at the Atmospheric Aerosol Surface*, sometimes computational results don't match initial predictions. How do you think about errors in calculations and system construction vs. chemically significant results? Do you always try to determine the underlying cause of an unforeseen result?

Zhu, C.; Kumar, M.; Zhong, J.; Li, L.; Francisco, J. S.; Zeng, X. C. New Mechanistic Pathways for Criegee–Water Chemistry at the Air/Water Interface. *J. Am. Chem. Soc.* 2016, 138, 11164–11169.

16. **EMMA:** You mentioned briefly at the end of the paper that previous studies would suggest that the stepwise mechanism might play an even more important role in other Criegee intermediate (not CH₂OO) water reactions at the air-water interface because the energy barrier for the reaction with water dimer (which we are assuming to mean the loop-mediated structure) may be higher for other Criegee intermediates. Did you do any calculations on the stepwise mechanism for other Criegee intermediates to determine how its activation barrier would change? If so, what is the reason for these higher energy barriers for the loop structure but not the stepwise mechanism for the other Criegee intermediate water reactions? If not, what leads you to believe that the stepwise mechanism may play an even more important role in the reaction of other Criegee intermediates with water at the air-water interface?
17. **ANIA:** The gas-phase AIMD simulations produced no reaction between CH₂OO and the water dimer in the entire 80 ps simulated time. It was concluded that the reaction time was longer than ~100 ps. Why did you run simulations that were only 80 ps in length, especially given the cited data from Anglada, et al. (Table S4, Anglada, J. M.; Sole, A. Impact of the water dimer on the atmospheric reactivity of carbonyl oxides. *Phys. Chem. Chem. Phys.* **2016**, 18, 17698) that suggest the shortest timescale would be on the order of 10³ ps? Is this influenced by using a different water system from the one used in Anglada et al.?
18. **NELL:** It is hard to visualize a clean monomer/dimer/trimer water with Criegee intermediate reaction occurring at the air-water interface because it would seem like there would always be more water molecules around that are interfering with the reaction. Are the loop-mediated structures in the reaction at the air-water interface ever cleanly only monomer/dimer/trimer reactions? The CH₂OO-water dimer loop structure is determined to be thermodynamically more favorable than the monomer reaction at the air-water interface, similar to the gas phase. Were you able to gain any insights into what chemical factors might be able to explain this? Is this driven by sterics, hydrogen bonding, stabilizing interfacial water molecules, or other factors?

Anglada, J. M.; Martins-Costa, M.; Ruiz-López, M. F.; Francisco, J. S. Spectroscopic Signatures of Ozone at the Air–Water Interface and Photochemistry Implications. *Proc. Nat. Acad. Sci. U.S.A.* 2014, *111*, 11618–11623.

19. **LUCY:** You mention how the observed shift in the absorption spectrum will be more relevant in optically thin clouds or just the tops of thicker clouds because of the light penetration– for reactions at the air-water interface that are not light-dependent. Small molecules are able to diffuse over long periods rather than be immediately absorbed (like light). Does this allow them to reach the interior of clouds, or are they preferentially absorbed at the edges of a cloud, despite the clouds being largely empty space? Are non-photochemical reactions also influenced by the position of a droplet inside of a cloud?
20. **EMMA:** The polarization effect from the highly asymmetric electric field at the interface “plays a very small role” in the O₃ spectroscopic shift. Does the asymmetric field describe the lack of hydrogen bonding at the air side of the air-water interface or is it describing a different interfacial process? How did you determine that the asymmetric field was not playing a large role in the observed shift?
21. **SEAN:** You mention that “the molecular properties of ozone are expected to exhibit large fluctuations, between gas-phase and bulk solution values” (11619) and that there is an increase in ozone dipole at the interface. Does this explain why hydrophobic ozone is most stable at the interface, or does the interface tend to stabilize hydrophobic species as well (since they aren't disrupting a complete hydrogen bond network)? Given the fluctuation in molecular properties, is a single new absorption spectrum for ozone at the air-water interface a good estimate of the effects across the entire interface?

Kumar, M.; Trabelsi, T.; Carlos Gómez Martín, J.; Saiz-Lopez, A.; Francisco, J. S. HIO_x-IONO₂ Dynamics at the Air-Water Interface: Revealing the Existence of a Halogen Bond at the Atmospheric Aerosol Surface. *J. Am. Chem. Soc.* 2020, *142*, 12467–12477.

22. **WILL:** For the minor channel, the O2 and I2 have a distance of 5.4Å (**Figure 1**) at the start of the simulation, whereas in the major channel the distance between O1 and I2 is 3.25Å (**Figure 2**). Does the larger initial distance between the atoms that will eventually halogen bond have an impact on the timing of the halogen bond formation (0.402 ps in the major channel and 0.794 ps for the minor channel) and contribute to the suggestion of weaker halogen bonding if longer bond distances indicate weaker bonds?

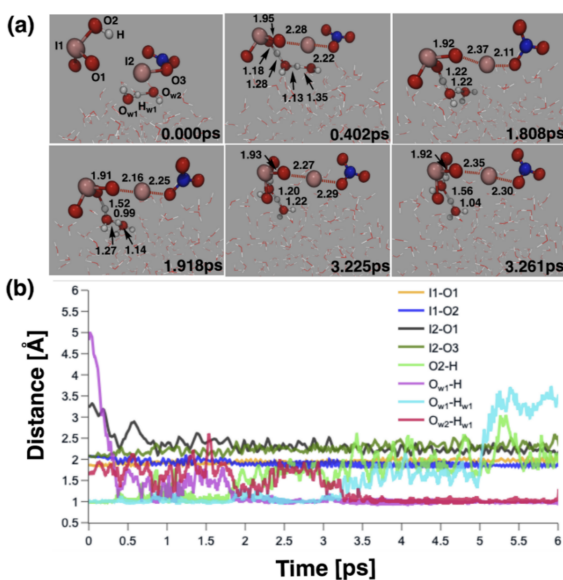


Figure 1. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between HIO₃ and IONO₂ at the air–water interface represented by a water droplet of 191 water molecules. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the HIO₃–IONO₂ interaction en route to halogen bond formation. Description of the dominant mechanistic channel that leads to halogen bond formation between HIO₃ and IONO₂ at the air–water interface.

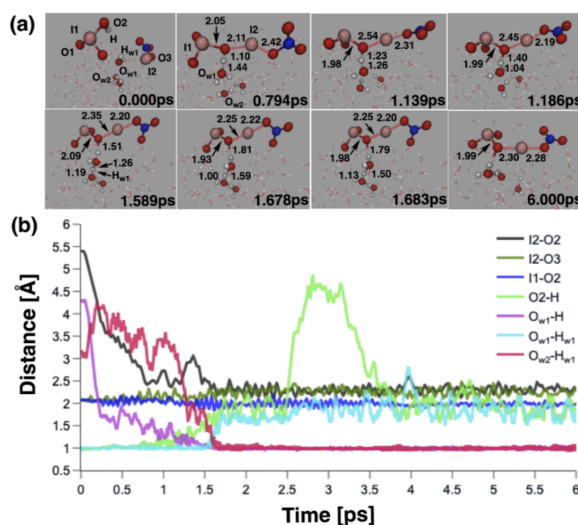


Figure 2. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between HIO₃ and IONO₂ at the air–water interface represented by a water droplet of 191 water molecules. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the HIO₃–IONO₂ interaction en route to halogen bond formation. Description of the minor mechanistic channel that leads to halogen bond formation between HIO₃ and IONO₂ at the air–water interface.

23. **WILLIAM:** In **Figure 4b**, the peak bond lengths of the oxygen-iodine bonds forming the halogen bond, I2-O1 (2.22 Å) and I2-O3 (2.32 Å), are different. What are the implications of these differences? Could it be a timescale effect because the I2-O3 bond was originally a covalent bond before the halogen bond was formed?

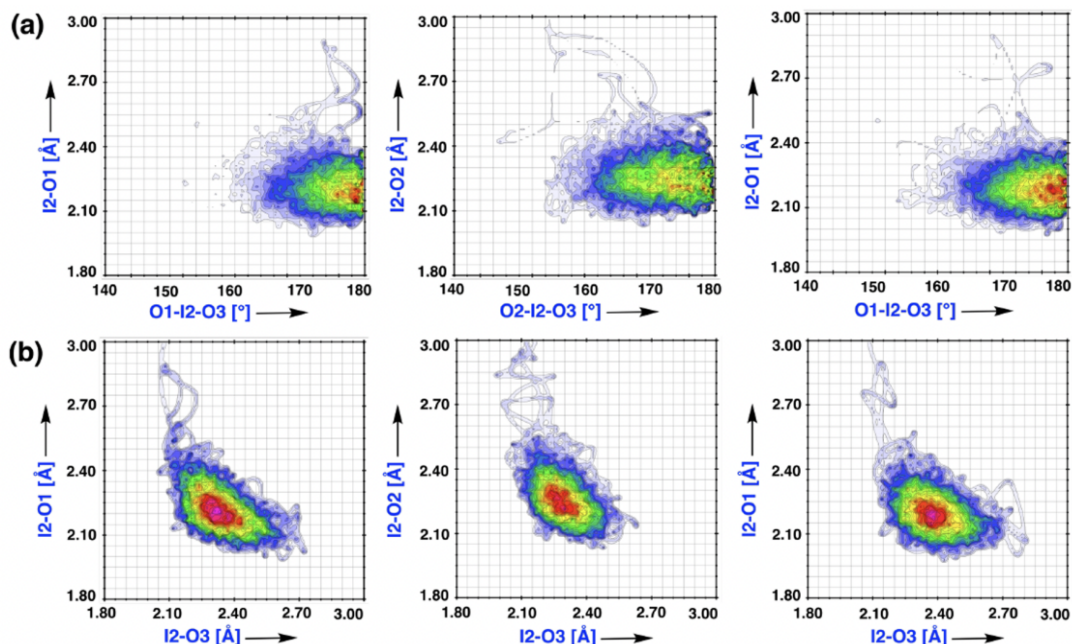


Figure 4. Combined radial/angular distribution function (CDF). The top panels show the CDFs involving a radial distribution function (RDF) between I₂ of the IONO₂ and O₁ or O₂ of HIO₃ (two left most panels) and O₁ of HIO₂ (extreme right panel) at the air–water interface and an angular distribution function between the I₂·O₃ and I₂·O₁ or I₂·O₂ vectors. The lower panels show the CDFs involving an RDF between I₂ and O₃ of the IONO₂ and an RDF between the I₂ of IONO₂ and O₁ or O₂ of HIO₃ (two left most panels) and O₁ of HIO₂ (extreme right panel).

24. **NORA:** Page 12471, column 2, paragraph 1 states that the CDFs in **Figure 4a** show that the peak halogen bonding angle for the major channel is about 178° and about 174° for the minor channel. This suggests that the halogen bonding in the minor channel is slightly weaker than the major channel, possibly due to the original readjustment that HIO₃ has to go through in the minor channel mechanism. However, there is only a 0.5 ps difference between when the halogen bond forms for the major channel versus the minor channel. How would the overall strength and stability of the peak halogen bonding angle be affected by the time taken for the rearrangement of those bonds at the beginning of the 40 ps simulation?

25. **LUCY:** In this paper, you observe the rotation of the oxygens around the C-S axis for the ion pair with MSA^- and CH_3NH_3^+ and $(\text{CH}_3)_2\text{NH}_3^+$ (**Figure 2b**). We would expect these oxygens to be chemically equivalent, but the rotations suggest that maybe they aren't. What is the driver for this rotation? Is the significance of this rotation that the oxygens are in fact chemically equivalent because the ion pair remains despite the rotation? Or does it imply that there is some difference that drives the single rotation seen in **Figure 2b** each time the ion pair forms?

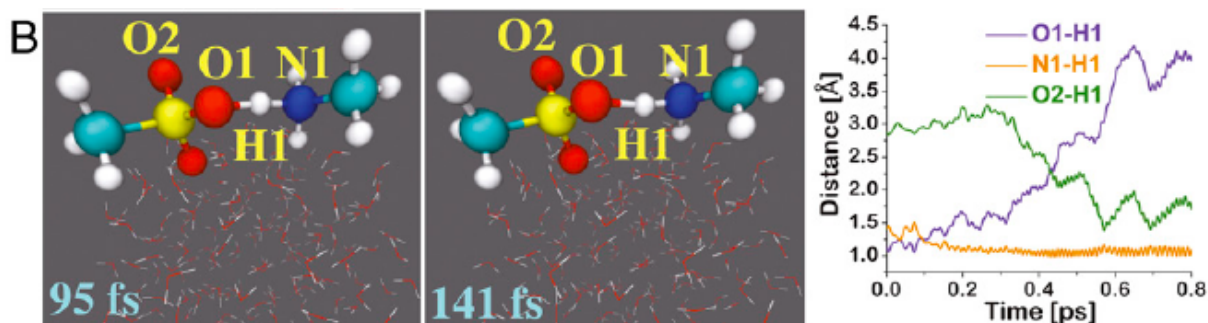


Fig. 2. (Left) Snapshot structures taken from the BOMD simulations for the reaction of HMSA with NH_3 and methylamine (CH_3NH_2), which illustrate the formation of $\text{MSA}^- \cdot \text{NH}_4^+$ (A) and $\text{MSA}^- \cdot \text{CH}_3\text{NH}_3^+$ (B) ion pairs on the water droplet. (Right) Time evolution of key bond distances O1-H1, O2-H1, and H1-N1 involved in the ion pair-forming reactions.

26. **ANIA:** The study found that the hydrogen-bonded complex between HMSA and the amine must be formed in the gas phase before the ion pair formation can occur at the interface (page 12402). Why must it be hydrogen bonded first in the gas phase for ion pair formation to occur? Could it be due to the fact that HMSA and amines would hydrogen bond to water molecules instead of forming an ion-pair? Is this still a limiting factor over longer timescales, or can the HMSA and amine eventually form a hydrogen bonded complex given enough time?
27. **NELL:** In **Table 1**, the number of hydrogen bonds are shown for the ion pair complexes formed by each of the three amines. In the case of the dimethylamine-HMSA ion pair, there are no longer any hydrogen bonds to the MSA^- , but the average number of the hydrogen bonds to the amine only decreases from 1.0 to 0.7. We were surprised by this, because the added hydrophobicity came from adding a methyl to the amine side of the ion pair. Why did increasing the hydrophobicity of the amine half cause more change to the solvation structure of the MSA^- half? Is it possible that sterics are involved with this trend? Based on **Table 1** and **Figure 4**, is the 30% of the $(\text{CH}_3)_2\text{NH}_2^+ \dots \text{MSA}^-$ ion pair that has zero hydrogen bonds able to escape into the gas phase? If not, what are the main takeaways of studying the hydration shell?

Table 1. Calculated average number of hydrogen bonds between $\text{MSA}^{\ominus}\cdots(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$ (for NH_3 , $\text{R}_1 = \text{R}_2 = \text{H}$; for CH_3NH_2 , $\text{R}_1 = \text{H}$ and $\text{R}_2 = \text{CH}_3$; and for CH_3NH_2 , $\text{R}_1 = \text{R}_2 = \text{CH}_3$) and interfacial water molecules

$\text{MSA}^{\ominus}\cdots(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$	Average no. of hydrogen bonds		
	Total	$(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$ bound	MSA^{\ominus} bound
$\text{R}_1 = \text{R}_2 = \text{H}$	4.1	1.9	2.2
$\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_3$	3.5	1.0	2.5
$\text{R}_1 = \text{R}_2 = \text{CH}_3$	0.7	0.7	0

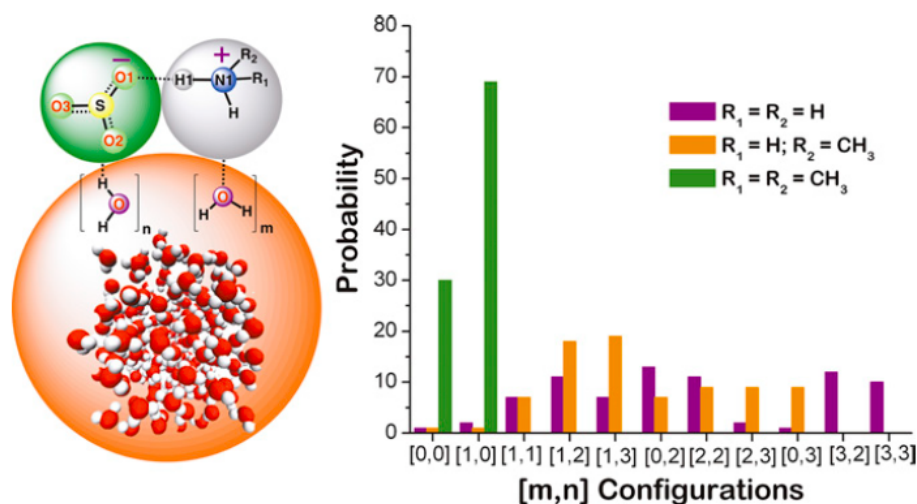
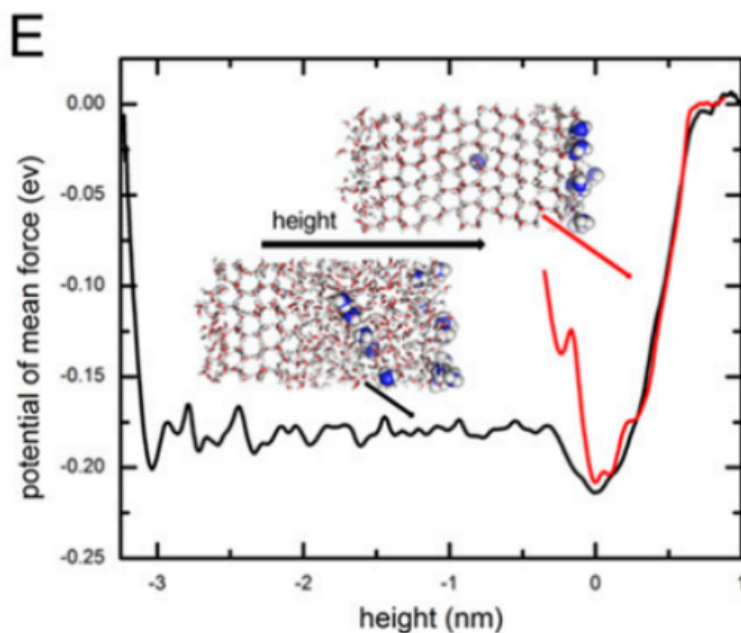


Fig. 4. (Left) Schematic showing the $[m,n]$ interfacial waters forming hydrogen bonds with ammonium or aminium protons and oxygens of $\text{MSA}^{\ominus}\cdots(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$ [for NH_3 , $\text{R}_1 = \text{R}_2 = \text{H}$; for CH_3NH_2 , $\text{R}_1 = \text{H}$ and $\text{R}_2 = \text{CH}_3$; and for $(\text{CH}_3)_2\text{NH}$, $\text{R}_1 = \text{R}_2 = \text{CH}_3$], where m and n are the numbers of interfacial water molecules bound to $(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$ and MSA^{\ominus} , respectively. (Right) Histograms of probabilities of different $[m,n]$ configurations for the $\text{MSA}^{\ominus}\cdots(\text{R}_1)(\text{R}_2)\text{NH}_2^{\oplus}$ particles (for NH_3 , purple; for CH_3NH_2 , orange; and for CH_3NH_2 , olive).

28. **EMMA:** Does the finding that ion pair formation can occur in the gas phase for all amines in the presence of only a single water molecule undermine the importance of the air-water interface results? In the case of ammonia and methylamine, hydrogen bonding with interfacial water suggests an interfacial contribution to the stability of ion pairs. Dimethylamine has the lowest number of hydrogen bonds (**Fig. 4**, above); can we infer that this ion pair is stable enough such that it does not need to be stabilized with interfacial water molecules? Is the geometry of this ternary complex analogous to the more complete hydration shells seen at the interface?

Ge, C.; Zhu, C.; Francisco, J. S.; Zeng, X. C.; Wang, J. A Molecular Perspective for Global Modeling of Upper Atmospheric NH₃ from Freezing Clouds. *Proc. Natl. Acad. Sci. U.S.A.* 2018, 115, 6147–6152

29. **SEAN:** Can this quasi-liquid layer scavenge ammonia in an area like the UTLS? Based on the potential of mean force curves shown in **Figure 1E**, the air-water interface still provides an energetic minimum relative to the gas phase and we know that ammonia will be easily scavenged by bulk water. After being ejected from frozen water droplets can the ammonia in the UTLS react with other species or does it get scavenged? At low altitudes, scavenging results in ammonia having a lifetime of a couple hours in the atmosphere. What is its lifetime in the UTLS region?



30. **WILLIAM:** The MIPAS and GEOS-Chem data include ammonia concentrations up through the altitude of 20 km (**Figure 4**), above where we would expect to find the UTLS. Can the ammonia concentrations at this height still be attributed to deep convection and monsoon height variance, or is it inconsistent with the collision mechanism proposed in the paper? At around 15 km in **Figure 4**, R=0 and R=0.05 switch from systematically overestimating ammonia concentrations to systematically underestimating them. What would be the benefits of more precisely trying to target a more accurate R value?

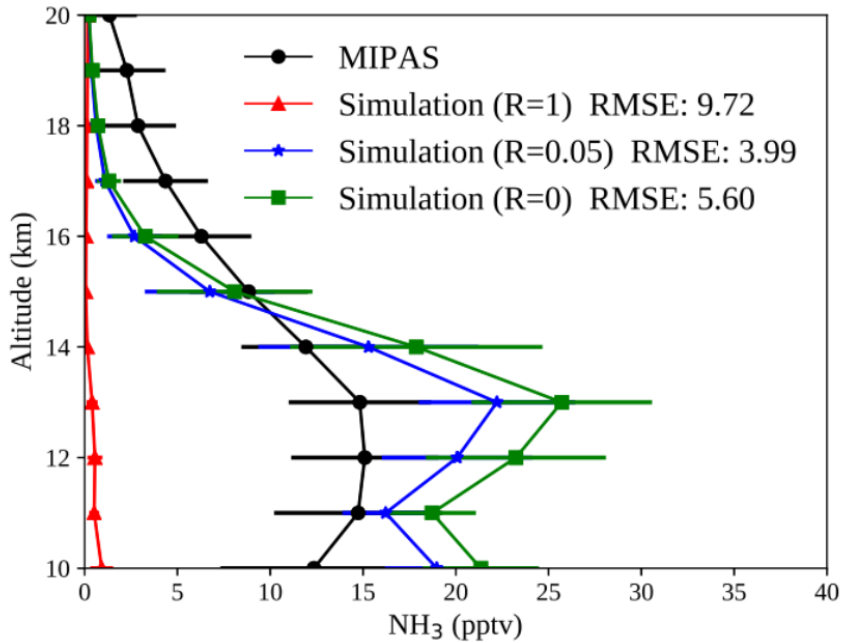


Fig. 4. Comparing the simulations with MIPAS-measured seasonal (June, July, and August) vertical profile of NH_3 over Asia over 6 y (2003 and 2007–2011). The profile of NH_3 volume mixing ratio is averaged over the eastern part of the Asian monsoon area ($30\text{--}40^\circ\text{N}$, $70\text{--}110^\circ\text{E}$). The NH_3 simulations are from the R1, R0.05, and R0 modeling results. The SDs are shown as error bars, and also shown are root mean squared error (RMSE).

31. **NORA:** What factors (data and simulations) helped you determine the collision hypothesis? Do collisions between ice particles release enough potential energy to overcome larger barriers than the relatively small barrier we see in the case of NH_3 ? Are there ways you could computationally model the collision process itself? What are the challenges in doing so and why did you not decide to try something similar for the paper?