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Exploring the Fate of Water Molecules Striking Concentrated Sulfuric Acid: Scattering versus Solvation

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Controlled collisions between gas-phase D_2O molecules and liquid sulfuric acid can provide valuable insights into hydrogen bonding, solvation, and protonation at the water vapor–acid interface.[1] When D_2O molecules strike a low vapor pressure liquid like H_2SO_4, they may scatter impulsively from the surface or bind momentarily to the acid molecules before desorbing or dissolving.[2,3] Each incident D_2O may also undergo proton exchange, either during the first few collisions or after solvation. These pathways can be probed by directing a beam of D_2O molecules at a fresh surface of H_2SO_4 in vacuum and monitoring the identities and velocities of the scattered products. We find that, despite concentrated sulfuric acid's extreme protonating and desiccating powers, D_2O molecules *can* survive collisions with the acid at incident energies spanning 6.4–66 kJ/mol. Almost all D_2O that survive scatter impulsively from the surface: those D_2O which interact strongly enough with the liquid to accommodate on the surface dissolve into the acid rather than desorb into the vacuum. The data also imply that solvation accompanies proton exchange and prevents the products from desorbing within the 0.05-s time scale of the experiment. We conclude that D_2O molecules either strike the acid in nonreactive trajectories, undergoing one or a few impulsive collisions before departing, or suffer enough collisions to dissipate their energy and dissolve for long times.

We scatter D_2O from 97.2–98.7 wt % H_2SO_4 (doubly distilled, GFS Chemicals), which is composed of neutral and ionic species dominated by hydrogen-bonded H_2SO_4 molecules.[4] The 1.5 wt % increase arises from vacuum distillation of the acid during the experiment. Clean liquid films at T_{liq} = 24 °C are prepared inside a vacuum chamber by partially immersing a glass wheel in a Teflon reservoir filled with the acid.[2] The wheel rotates at 0.5 Hz, picking up a 0.7-mm-thick film. A glass blade scrapes away the outermost 0.5 mm of the acid, exposing a fresh, 0.2 mm thick liquid layer. This continuously moving film passes by a 12-mm-diameter hole, where it intercepts beams of D_2O for 0.05 s. The translational energies of the recoiling D_2O are determined from time-of-flight (TOF) spectra, which register the time for scattered species to travel 19.4 cm from a chopper wheel to a mass spectrometer. Molecular beams of D_2O are generated by bubbling N_2, He, or H_2 through D_2O at 0 °C and expanding the gas mixture through a pinhole. The translational energies $E_i \pm \sigma_E$ of the incident D_2O beams are 6.4 ± 1.1, 29 ± 4, and 66 ± 5 kJ/mol, corresponding to 1.3, 6, and 13 times the average translational energy of D_2O molecules at 24 °C. For comparison with D_2O collisions, we also scatter neon atoms from the acid at energies of 6.3 ± 0.5 and 61 ± 4 kJ/mol. We estimate that the film is exposed to less than 0.02 monolayers of D_2O as it passes by the hole.

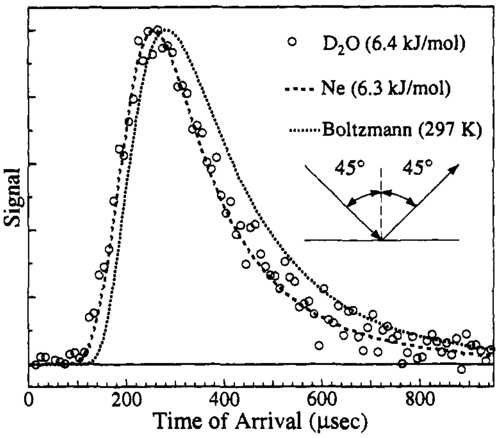

Figure 1. Time-of-flight spectra of low-energy D_2O and Ne scattering from H_2SO_4 at incident and exit angles of 45°. A Boltzmann distribution is shown for comparison. The peak heights are arbitrarily normalized to 1.

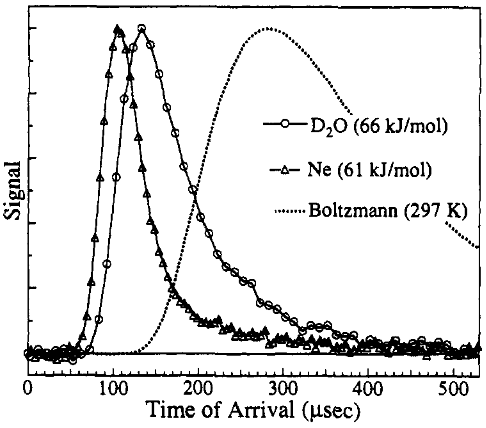

Figure 2. Time-of-flight spectra of high-energy D_2O and Ne scattering from H_2SO_4. The solid lines connect the data points.

Figure 1 shows TOF spectra of low-energy D_2O and Ne scattering from H_2SO_4. The measurable D_2O signal demonstrates that some water molecules colliding at thermal energies can recoil from the surface rather than react with the acid. The surviving D_2O depart with velocities nearly equal to those of neon atoms at similar collision energies, and they are faster than predicted by thermal desorption at T_{liq}. Figure 2 shows that, at higher energies, D_2O and Ne scatter in sharp, nonthermal velocity distributions. In each figure, the D_2O resemble inert gas atoms of equal mass undergoing one or a few billiard ball-like collisions with the acid molecules.[2,3] On average, the high-energy Ne and D_2O lose 50% and 71% of their incident energy upon collision. The larger energy loss for D_2O reflects the stronger attractive forces between D_2O and H_2SO_4 and the excitation of rotational and possibly vibrational modes of D_2O.

Depletion experiments demonstrate that a significant fraction of the D_2O disappears into the acid. We have crudely measured the sticking probability $S = (P_F - P_A)/(P_F - P_B)$, where P_F, P_A, and P_B are the D_2O background pressures when the incident beam strikes a Teflon flag, strikes the acid, and is blocked from entering the chamber, respectively. S equals 1 for complete sticking and 0 for complete scattering. The S values at normal incidence lie between 0.3 and 0.8 at E_i = 6.4 kJ/mol and between 0.25 and 0.65 at 66 kJ/mol. The measurements are not reproducible enough to report more precise values, but they serve to complement Figures 1 and 2 by showing that some D_2O dissolve into the acid rather than scatter from the surface.

The pathway we observe for solvation is illustrated Figure 3 for high-energy collisions of D_2O with H_2SO_4 and with glycerol, a weakly acidic alcohol. The fast peak in the glycerol spectrum consists of D_2O scattering impulsively from the surface, while the slow peak arises from thermal desorption of D_2O that have

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(1) For related studies, see: Davidovits, P.; Jayne, J. T.; Duan, S. X.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1991**, *95*, 6337–6340 and references therein.

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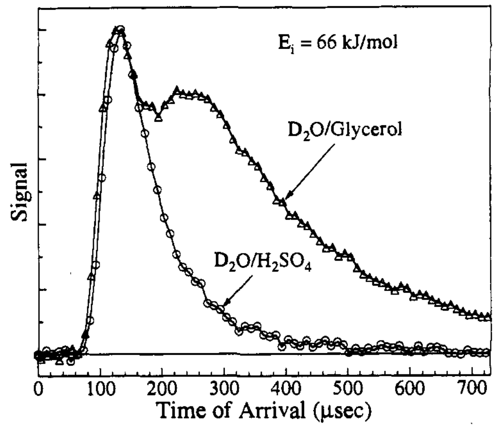

Figure 3. Time-of-flight spectra of D_2O scattering from H_2SO_4 and glycerol.

accommodated on the surface or dissolved momentarily in the alcohol. This thermal desorption peak is typically observed in collisions between D_2O and nonreactive liquids, including squalane and perfluorinated ethers.[2] The fast D_2O recoil at similar velocities from H_2SO_4 and from glycerol, reflecting the similar masses of the two molecules and their common OH groups. However, the trapping–desorption peak which dominates the glycerol spectrum is nearly absent when D_2O strikes H_2SO_4. The missing desorption peak in the H_2SO_4 spectrum implies that D_2O molecules which interact strongly enough with the acid to dissipate their energy and thermalize must dissolve rather than desorb. Figure 3 suggests that trapping is almost always followed by solvation in high-energy collisions of water molecules with concentrated sulfuric acid. Figure 1 also suggests that the D_2O which survive are those which scatter impulsively: the water molecules recoil with neon atom-like velocities and do not depart in a thermal distribution, in direct contrast to the thermal desorption of low-energy D_2O striking glycerol.[2]

Proton exchange between D_2O and H_2SO_4 appears to occur after or immediately before the water molecules dissolve in the acid. On the basis of the acid's Hammett acidity[4] of less than -10 and picosecond time scales for protonation,[5] we expect that all solvated D_2O will exchange D for H within the 0.05-s time window. We observe at E_i = 29 kJ/mol that the scattered HOD signal is 3.0 ± 0.5% of the D_2O signal, which we attribute to the 4.0 ± 0.5% HOD contamination in the incident beam. A high detector background prevents measurements of H_2O arising from double proton exchange. However, to within an estimated statistical uncertainty of 20% (2σ) of the incident beam flux, we observe no extra D_2O when H_2O strikes 98 wt % D_2SO_4. The absence of detectable, single-proton-exchanged water indicates that there are few direct proton transferring collisions. Most D_2O which undergo proton exchange remain within the acid for at least 0.05 s.

We acknowledge the possibility that an impurity layer on the surface may deflect some incoming D_2O back into the gas phase and enhance the signal. Acid surface tensions before and after the experiment, however, lie within 1 dyn/cm of literature values, implying that there is little contamination of the surface. In addition, some incoming D_2O may scatter from evaporating molecules just above the surface. For 97 wt % H_2SO_4, the total vapor pressure of 3×10^{-4} Torr is 90% H_2O. Assuming a 100-Å^2 cross section for H_2O–D_2O collisions[6] that prevent the D_2O from reaching the acid, we predict that 3% or less of the low-E_i D_2O are deflected away.[2] This estimate is tested by cooling the acid to 15 °C, which reduces the vapor pressure 3-fold. The scattered D_2O signal does not decrease upon cooling, as it would if gas-vapor scattering were significant.

The TOF results suggest that water molecules which dissipate their energy upon collision with the surface remain long enough to reach configurations where they can bind to the acid molecules and diffuse into the liquid. Energy transfer will occur through one or several collisions, depending on the local configurations of the surface H_2SO_4, the orientation of the D_2O, and the point of impact. Glancing blows may propel the D_2O away from the surface, while head-on impacts and encounters with a rough surface created by loosely packed H_2SO_4 will promote multiple collisions and extensive energy transfer.[3] This energy exchange is enhanced when the D_2O are accelerated into the acid molecules by attractive forces between the base and the acid, including dispersion, dipolar, and hydrogen-bonding/charge-transfer interactions.[7]

Within this picture, we imagine that some D_2O molecules will behave like inert gas atoms if they follow glancing or single collision trajectories, particularly if they are not aligned to hydrogen bond or if they encounter surface H or O atoms of H_2SO_4 already hydrogen bonded to other H_2SO_4. These D_2O scatter impulsively from the surface and do not react. In contrast, the multiple collisions that drain away the D_2O's incident energy appear to detain the D_2O molecule long enough for it to enter the liquid, perhaps aided by hydrogen bonding with surface H_2SO_4. D_2O protonation most likely occurs when the D_2O is surrounded by enough H_2SO_4 molecules to solvate the resulting ions,[1,8] prolonging dissolution for at least 0.05 s. Water molecules striking glycerol may initially follow similar pathways, but the D_2O desorb from the alcohol before being protonated.[2]

These experiments suggest that, unlike solute molecules trapped within the acid's interior, soluble molecules striking the liquid's surface may escape solvation after one or several collisions with the acid molecules. The acid's surface may thus limit the rates of bulk solvation and protonation by restricting energy transfer and thermal accommodation of the impinging water molecules.

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