Uptake of \( \text{N}_2\text{O}_5 \) by aqueous aerosol unveiled using chemically accurate many-body potentials

Vinicius Wilian D. Cruzeiro\(^1,2\), Mirza Galib\(^3\), David T. Limmer\(^3,4,5,6\) & Andreas W. Götz\(^1\)

The reactive uptake of \( \text{N}_2\text{O}_5 \) to aqueous aerosol is a major loss channel for nitrogen oxides in the troposphere. Despite its importance, a quantitative picture of the uptake mechanism is missing. Here we use molecular dynamics simulations with a data-driven many-body model of coupled-cluster accuracy to quantify thermodynamics and kinetics of solvation and adsorption of \( \text{N}_2\text{O}_5 \) in water. The free energy profile highlights that \( \text{N}_2\text{O}_5 \) is selectively adsorbed to the liquid–vapor interface and weakly solvated. Accommodation into bulk water occurs slowly, competing with evaporation upon adsorption from gas phase. Leveraging the quantitative accuracy of the model, we parameterize and solve a reaction–diffusion equation to determine hydrolysis rates consistent with experimental observations. We find a short reaction–diffusion length, indicating that the uptake is dominated by interfacial features. The parameters deduced here, including solubility, accommodation coefficient, and hydrolysis rate, afford a foundation for which to consider the reactive loss of \( \text{N}_2\text{O}_5 \) in more complex solutions.
The uptake of trace gases from the air into aerosol particles impacts a wide range of environmental systems. Among other things, such multiphase processes help to determine the oxidative power of the atmosphere by acting as sinks for nitrogen oxides. Of particular long-standing interest is the reactive uptake of N2O5 in aqueous aerosol, which is estimated to account for 15–50% of the loss of NOx in the troposphere. Despite the significant study, basic questions remain concerning the mechanism of N2O5 uptake. Molecular dynamics simulations can be used to obtain a molecular perspective on gaseous uptake, free of underlying rate limitation assumptions. However, studying such processes theoretically imposes challenges, since uptake coefficients are exponentially sensitive to free energy differences and the simulations involve large systems and long times to model the complex dynamics. While qualitative predictions of mechanisms can be typically studied with conventional empirical force fields or density functional theory-based models, quantitative predictions require higher levels of accuracy. To address this challenge, a many-body potential, MB-nrg, has recently been parameterized from coupled-cluster calculations, providing the capability of making quantitative predictions of the thermodynamics and kinetics leading to the N2O5 uptake.

Gaseous uptake into fluid particles couples thermodynamic constraints of solubility with kinetic details of reaction and diffusion. As a complete analytical analysis of the appropriate reaction–diffusion equations is not typically tenable, approximate models are commonly postulated employing a small number of thermodynamic and kinetic properties. For example, the uptake of N2O5 in aqueous aerosol has been assumed to follow such a model, determined by bulk accommodation followed by bulk phase hydrolysis and parameterized by its bulk solubility and hydrolysis rate. Such kinetic models typically lack molecular details, neglecting the finite width of the liquid–vapor interface and its potential unique properties. With molecular dynamics simulations these assumptions can be relaxed, and the relevant parameters extracted to inform an atomistic kinetic model. Further, by solving the reaction–diffusion equations numerically, the simplified models can be refined.

The validity of the traditional resistor model for the reactive uptake of N2O5 has been recently called into question due to the difficulty of reconciling the kinetics with field measurements, combined with theoretical work providing indications of interfacial stability and reactivity. The mechanism of uptake has been recently explored directly using a neural network-based reactive model, and it was found that interfacial rather than bulk phase processes dictate the observed uptake coefficient. Using training data obtained from density functional theory, this study found that the hydrolysis rate was sufficiently fast at the interface that bulk phase partitioning cannot kinetically compete, and the uptake was determined by a competition between interfacial hydrolysis and vaporization. These calculations found modest agreement with experimental uptake coefficient values, consistent with the expected qualitative accuracy of the model employed. As direct experimental confirmation of the importance of the interface is difficult, an alternative means of validating it is to employ models with higher chemical accuracy. This is the aim of the current work, to apply a quantitatively accurate potential to extract the thermodynamic and kinetic properties underpinning the uptake of N2O5 into water.

MB-nrg potentials can serve to make a quantitative prediction of gaseous uptake as they can be accurate yet computationally amenable to the large system sizes and long timescales required to simulate interfacial processes just like the MB-pol water model. Contrary to common neural network models, these many-body potentials have an explicit representation for long-range interactions, which can be important at extended interfaces. For example, it has been shown that MB-pol yields quantitative accuracy for a variety of molecular properties across water’s phase diagram including at the water–vapor interface. Extensions of this modeling framework to describe mono-atomic ions and small molecules in aqueous solutions as well as generic mixtures of molecules have been recently realized. These MB-nrg models include a model of N2O5 that has been developed using analogous approaches. This MB-nrg model was demonstrated to yield comparable accuracy with respect to the coupled cluster reference data it was parameterized on, enabling highly accurate simulations of N2O5 in aqueous environments. While not able to describe reactions with water, the model nevertheless is capable of quantifying the processes that establish the physical uptake of N2O5.

Here we employ this MB-nrg model to study the physical uptake of N2O5 into water using molecular dynamics simulations and enhanced sampling techniques, making quantitative predictions of the thermodynamics and kinetics of N2O5 uptake. We subsequently leverage the quantitative accuracy of the model to parameterize and solve a reaction–diffusion equation and infer hydrolysis rates consistent with experiment, providing a complete quantitative picture of the reactive uptake of N2O5 by aqueous aerosol. We find a short reaction–diffusion length, indicating that the uptake is dominated by interfacial features in the vicinity of the liquid–vapor interface.

**RESULTS**

In order to extract the thermodynamic and kinetic properties that determine the uptake of N2O5, we have simulated a system containing a slab of liquid water in contact with its vapor and a single N2O5 molecule as described in the Methods section and illustrated in Fig. 1a. The corresponding density profile of water along the direction perpendicular to the interface, ρ(z), is shown in Fig. 1b, exhibiting the expected sinusoidal profile consistent with emergent capillary waves. The bulk density of the MB-pol model ρ0 is 1.007 g/cm3. We take the origin of z to be coincident with the Gibbs dividing surface of the interface.

**Thermodynamics of adsorption and solvation.** Using this simulation setup, we first considered the thermodynamics of N2O5 solvation in liquid water. Figure 1c shows the free energy profile for moving a gaseous N2O5 into liquid water. Supplementary Fig. 1 depicts the free energy profile in more detail and the Supplementary Notes and Supplementary Table 1 contain an overview of all thermodynamic and kinetic parameters discussed in this text. For both z ≫ 0 and z ≪ 0, the free energy profile is flat, reflecting the translationally invariant bulk liquid and vapor on either side of the interface. We define the offset between these asymptotic values as βΔFle = −4.3 ± 0.1, the solvation free energy for the gas phase N2O5, where β = 1/k_BT and k_B is Boltzmann’s constant. In between these two extremes, the free energy is non-monotonic and exhibits a global minimum approximately centered at the Gibbs dividing surface of the interface.

Relative to the gas phase, the global minimum corresponds to an interfacial adsorption free energy of βΔFle = −6.2 ± 0.1. The interfacial adsorption indicates N2O5 is relatively hydrophobic, consistent with previous observations of its relatively weak solvation. This free energy profile dictates that the equilibrium density profile of N2O5 would be inhomogeneous in the vicinity of the liquid–vapor interface, a feature neglected in typical kinetic models.

**Solubility.** From the free energy profile we can calculate the solubility of N2O5 in liquid water. In dilute solution at
Using the known experimental viscosity of liquid water at ambient conditions\textsuperscript{29}, we can correct for these finite size effects resulting in a diffusion constant in the thermodynamic limit of $1.89 \pm 0.06 \times 10^{-3}$ cm\textsuperscript{2}/s. We have also estimated the change in the diffusion constant at the liquid–vapor interface\textsuperscript{39}, and find an increase from its bulk value to $(5.3 \pm 0.1) \times 10^{-3}$ cm\textsuperscript{2}/s.

**Adsorption and evaporation rates.** Evaporation from the liquid–vapor interface and solvation into the bulk are both activated processes with barriers estimated from the free energy in Fig. 1 to be larger than typical thermal values. As such, they are rare events and difficult to sample with straightforward simulations. However, as we consider a system whose dynamics satisfies detailed balance, we can alternatively study comparatively typical events like desolvation and adsorption, and infer their reverse using the previously evaluated free energy profile\textsuperscript{26}. Definitions for these different dynamical processes are well described in ref.\textsuperscript{17}.

To compute the adsorption and therefore evaporation rates, we have sampled 250 scattering trajectories whereby an initially gas phase N\textsubscript{2}O\textsubscript{5} placed at $z = 1.2$ nm, shown in the right panel of Fig. 2a, is evolved toward the liquid slab. To do this we take 10 distinct equilibrium configurations of N\textsubscript{2}O\textsubscript{5} generated by constraining its center of mass to $z = 1.2$ nm, and draw 25 realizations of a Maxwell–Boltzmann distributed velocity at 300 K for each. Figure 2b reports the trajectories of the center of mass of the N\textsubscript{2}O\textsubscript{5} as it impinges on the liquid slab. Overwhelmingly, the incipient gas phase N\textsubscript{2}O\textsubscript{5} molecule meets the interface and sticks, with only 11 out of the 250 scattering trajectories exhibiting a back scattering event, with N\textsubscript{2}O\textsubscript{5} bouncing off of the interface and going back into the gas phase within the 100 ps observation time employed. The scattering rate is quantified with the so-called thermal accommodation coefficient, $S = 0.96 \pm 0.06$, relating the probability of being accommodated at the interface upon collision, consistent with previous simulations\textsuperscript{15}. This is likely a lower bound as some of the back scattering events can be attributable to equilibration at the interface followed by subsequent evaporation. The near unity value implies a lack of a barrier to adsorption, that subsequent evaporation is analogously limited only by the free energy of adsorption, and that uptake is not significantly influenced by this initial thermal accommodation. The corresponding rates of adsorption, $k_a$, and evaporation, $k_e$, can be computed from kinetic theory\textsuperscript{17}. Specifically, the rates are given by

$$k_a = S \frac{v}{4}, \quad k_e = k_a e^{-\beta \Delta F_s},$$

where $v = \sqrt{8/\beta \pi m}$ is the average molecular speed of N\textsubscript{2}O\textsubscript{5}. These are $k_a = 57$ nm/ns and $k_e = 0.11$ nm/ns.

**Solvation and desolvation rates.** We have also computed the rates of solvation and desolvation following the Bennet-Chandler approach\textsuperscript{37}. Identifying $z^i = -0.42$ nm as the location of the putative transition state for solvation into the bulk liquid from the interface (see Fig. 1c), we can estimate the rate of solvation and analogously desolvation by computing the transmission coefficient, $\kappa$, for committing to the interface conditioned on starting at the transition state. The transmission coefficient is defined as \textsuperscript{37}

$$\kappa(t) = \frac{(2\pi)^\lambda [z(t) - z^i]_+}{(|v|)_{\lambda}^2},$$

where $\Theta$ is the step function and the brackets denote an ensemble average where in the numerator it is conditioned on starting at the transition state. We have evaluated the transmission coefficient using 2000 trajectories. Like the scattering calculations, we...
Reactive uptake through interfacial and bulk hydrolysis. Experimentally, \( \text{N}_2\text{O}_5 \) undergoes facile irreversible hydrolysis with water and this reaction ultimately determines the reactive uptake in aqueous aerosol. While we cannot simulate the reactive event with the MB-nrg potential employed directly, we can still make an inference into the reactive uptake. Using the thermodynamic and kinetic parameters evaluated from the molecular dynamics simulations, we can parameterize a molecularly detailed reaction–diffusion equation. Specifically, we consider the diffusive dynamics accompanying an initially adsorbed \( \text{N}_2\text{O}_5 \) molecule as it enters the bulk liquid or evaporates, and address what would happen if it were able to also undergo hydrolysis.

Consistent with the near unity thermal accommodation \( S \), we assume an initially adsorbed molecule locally equilibrated at the interface. The subsequent evolution of its concentration profile, \( c(z, t) \), can be solved for using a Smoluchowski equation \(^{59} \)

\[
\frac{\partial c(z, t)}{\partial t} = \nabla \cdot \left( D(z) \nabla c(z, t) \right) - k_b(z) c(z, t) + k_d(z) c(z, t)
\]  (6)

where \( \Delta F(z) \) is the free energy profile from Fig. 1c, \( D(z) \) is the diffusion constant, and \( k_b(z) \) is the unknown hydrolysis rate, both of which in principle vary through space \(^{60,61} \). The first term is a drift diffusion encoding the stationary distribution implied by the free energy profile, while the second accounts for loss due to reaction. In practice, we fit the free energy to an analytic function form, \( \beta \Delta F(z) = a_1 \tan h[(z - a_2)/a_3] - a_4 \exp[-(z - a_5)^2/a_6] + a_7 \exp[-(z - a_8)^2/a_9] \). Equation (6) is valid only for the liquid and interface, not the vapor, since it is overdamped \(^{59} \). In order to model the vapor, we employ absorbing boundary conditions \( c(z = 1 \text{ nm}, t) = 0 \), and consider a domain that extends deeply enough into the liquid that the results are insensitive to the reflecting boundary condition employed there, \( \partial c(z = -30 \text{ nm}, t) = 0 \). We solve Eq. (6) with a normalized Gaussian initial condition, localized in the free energy minima near the Gibbs dividing surface where a standard deviation of 0.05 nm was found to well approximate the curvature of the interfacial minima. In practice, we employ a simple finite difference scheme with constant grid spacing of 0.02 nm and timestep 0.018 ps.

In the absence of any reactions, an initial interfacial concentration of \( \text{N}_2\text{O}_5 \) will relax through a competition between diffusion into the bulk liquid and evaporation into the vapor towards the steady-state determined by the free energy profile. Figure 3a illustrates the relaxation of this concentration profile. The initial Gaussian distribution quickly loses amplitude and a diffusive front propagates into the bulk liquid, while concentration is irreversibly lost to the vapor. The initial rates to evaporate and solvate are consistent with our explicit molecular simulation calculations. In the presence of hydrolysis, in addition to loss from evaporation, there can be loss due to reaction. Since the concentration is normalized to 1, the overall reactive uptake, \( \gamma \), can be computed by the portion of the loss through the reactive channel,

\[
\gamma(t) = \int_0^t dt' \int dz k_b(z) c(z, t')
\]  (7)

We model the hydrolysis rate as having two characteristic values, one in the bulk for \( z < 0.5 \text{ nm} \), denoted \( k_0 \), and one at the interface for \( -0.5 < z < 0.5 \text{ nm} \) taken to be a fraction of the bulk value, while it is set to zero in the vapor for \( z > 0.5 \text{ nm} \). The interfacial region was determined from the inflection points in the free energy curve and numerical tests have shown that the results are insensitive to the precise width of the interfacial region. An example time series for the reactive uptake is shown in Fig. 3b, which rises from 0 to a plateau value at times much longer than

\[
\alpha = \frac{S}{1 + e^{\beta \Delta F(z) + \Delta \gamma}}
\]  (5)

We find \( \alpha = 0.93 \pm 0.06 \), in agreement with experiments that infer a value larger than 0.4 for \( \text{N}_2\text{O}_5 \)^{58}.

Mass accommodation. We can also evaluate the mass accommodation coefficient \( \alpha \), defined as the probability of a gas molecule striking the liquid surface to solvate into the bulk liquid phase in absence of surface reactions\(^ {17} \). This fundamental parameter determines the transfer rate of \( \text{N}_2\text{O}_5 \) across the surface into the bulk liquid and can be computed from the sticking coefficient \( S \) and the free energy profile as

\[
\alpha = \frac{S}{1 + e^{\beta \Delta F(z) + \Delta \gamma}}
\]  (5)

We find \( \alpha = 0.93 \pm 0.06 \), in agreement with experiments that infer a value larger than 0.4 for \( \text{N}_2\text{O}_5 \)^{58}.

---

**Fig. 2 Kinetics of \( \text{N}_2\text{O}_5 \) adsorption and solvation.** a Snapshots of \( \text{N}_2\text{O}_5 \). Adsorption and evaporation takes \( \text{N}_2\text{O}_5 \) between the vapor (right) and interface (center), while solvation and desolvation takes it between the interface and the bulk (left), with corresponding rate constants. b Scattering trajectories following the \( z \) component of the center of mass of \( \text{N}_2\text{O}_5 \). c Transmission coefficient for transitions between the liquid and the interface. The shaded region are one standard deviation error bars. The solid red line is an exponential fit.

---

\( k_d \) as

\[
k_d = \frac{\nu}{2\ell} e^{\beta \Delta F_b}, \quad k_s = k_d e^{\beta (\Delta F_z - \Delta F_z)}
\]  (4)

where \( \beta \Delta F_b = 0.8 \) is the barrier to move from the bulk liquid to the interface and \( \ell = 0.6 \text{ nm} \) is the width of the interface. The width of the interface is determined by fitting the free energy minima to a parabola and integrating the resultant Gaussian distribution from 1 nm > \( z > z_1 \). We find \( k_d = 340/\text{ns} \) and \( k_s = 51/\text{ns} \).
The characteristic time associated with the bulk hydrolysis rate. This asymptotic value is the reactive uptake coefficient.

The reactive uptake as a function of the bulk hydrolysis rate is shown in Fig. 3c. For each bulk hydrolysis rate, we have computed γ setting the interfacial rate equal to k₀/5. Asymptotic uptake coefficients without (orange squares) and with (blue circles) interfacial reactivity. Blue regions denote the range of uptake coefficients observed experimentally on pure water, and gray the corresponding likely range of bulk hydrolysis rates.

Implications for the reactive uptake mechanism. Apart from quantifying a likely range of experimental hydrolysis rates, the analysis of the reaction–diffusion model provides insight into the likely mechanism of reactive uptake. Specifically, the range of uptake values observed upon changing the interfacial hydrolysis rate from 0 to k₀ illustrates that, while interfacial reactivity contributes to the reactive uptake coefficient, it accounts for at most 20%. The interfacial contribution is lower than recent estimates, due to the increased solubility predicted by the MB-nrg model and corresponding higher accommodation coefficient relative to the previous neural network model study. Nevertheless, a significant adsorption-free energy reduces diffusion into the bulk liquid, resulting in an effective renormalized reaction–diffusion length. Absent barriers to solvation, the reaction–diffusion length, ℓ = D/k₀, would be around 15 nm. However, the barrier to solvation and corresponding free energy minima at the interface results in a propagation length of N₂O₅ into the bulk fluid of only around 2 nm (see Fig. 3a). This implies that reactive uptake is affected by interfacial characteristics, even though most of the reaction is predicted to take place in the bulk. It also predicts a very weak aerosol particle size dependence to reactive uptake consistent with some experimental observations.

Discussion

We report extensive molecular dynamics simulations with many-body potentials of coupled cluster accuracy that quantify the thermodynamics and kinetics of adsorption and solvation of N₂O₅ by aqueous aerosol. The hydrolysis rate of N₂O₅ is determined by numerically solving a molecularly detailed reaction–diffusion equation that incorporates these parameters to yield results consistent with the experimentally observed reactive uptake coefficient. This provides a complete quantitative picture of the reactive uptake of N₂O₅ by aqueous aerosol. Although most of the hydrolysis is predicted to take place in bulk water, our results highlight the importance of interfacial features at the liquid/vapor interface leading to a relatively short reaction–diffusion length and thus only very weak aerosol particle size dependence.

The framework and parameters determined here can be used as a new starting point for further modeling efforts to predict the reactive uptake of N₂O₅ in more complex solutions. It is well known that the reactive uptake can be modulated in the presence of inorganic salts, as in the case of excess nitrate ions. By quantifying the changes to both the thermodynamic and kinetic properties of N₂O₅ in the presence of these alternative solutions, advanced molecular models such as the ones used in this work in combination with similar analysis of generalized reaction–diffusion equations incorporating alternative loss mechanisms, can be exploited to provide a complete picture of reactive uptake of N₂O₅ with the full complexity of field measurements.

METHODS

Molecular dynamics simulations. To simulate the uptake of N₂O₅ in water we employed the MB-nrg model of N₂O₅ in MB-pol water with explicit one-body, two-body, and three-body short-range interactions. The simulation system

![Figure 3](image-url)
illustrated in Fig. 1a is made up of 533 water molecules forming a liquid slab measuring 2.416 nm × 2.416 nm in cross-sectional area and 2.772 nm in length. For this slab size, finite size corrections to thermodynamic properties are expected to be minimal. The system is embedded in a simulation domain of the same cross-section and a length of 20 nm in order to accommodate periodic boundary conditions. Simulations were executed with Amber 2020 interfaced to the MBX library. Ewald summation was employed to describe long-range electrostatics and dispersion interactions using a real-space cutoff of 1.2 nm. Thermodynamic averages were computed within an ensemble of fixed N particles, V volume, and T = 300 K temperature, using a Langevin thermostat and a timestep of 0.5 fs. Kinetic properties were evaluated within a constant energy ensemble with fixed N and V.

**Umbrella sampling.** We computed the free energy to move a gaseous N2O5 into the liquid water slab using umbrella sampling applied to the center of mass distance along the z direction between the water slab and N2O5. We employed harmonic biasing potentials of the form $\Delta U(z) = k(\frac{1}{2} - z^2)$ with a spring constant k of 2.5 kcal mol$^{-1}$ Å$^{-2}$ and 52 independent windows with minima $z_0$ spaced evenly between $\pm 1.36$ and 1.19 nm. Three separate sets of calculations were run, each consisting of 1 ns equilibration time followed by 2.5 ns production time to compute partial histograms. The individual histograms from each window were combined using umbrella integration. Error bars of the free energy profile were computed from the standard deviation for the three independent calculations.

**Diffusion coefficients.** Diffusion coefficients were computed from simulations of N2O5 in bulk liquid water. Details of the calculation of diffusion coefficients from mean-squared displacements in the molecular dynamics simulations are discussed in the Supplementary Methods.

**Data availability**

Data supporting the findings of this study are included in the article and a Source Data file is provided with this paper. In addition, the data related to this publication including simulation input files can be accessed from the NSF-CAICE Data Repository.

**Code availability**

This study utilized Amber 20 interfaced to MBX (http://paengroup.ucsd.edu/software/mbx.html). The software for solving the reaction–diffusion model is included in the Supplementary Material and can be accessed from the NSF-CAICE Data Repository.

Received: 20 September 2021; Accepted: 28 January 2022; Published online: 10 March 2022

**References**

1. Peter, T. Microphysics and heterogeneous chemistry of polar stratospheric clouds. Annu. Rev. Phys. Chem. 48, 785–822 (1997).
2. Finlayson-Pitts, B. J. & Pitts Jr, J. N. Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications (Elsevier, 2000).
3. Ravishankara, A. Heterogeneous and multiphase chemistry in the troposphere. Science 276, 1058–1065 (1997).
4. Pöschl, U. & Shiraiwa, M. Multiphase chemistry at the atmosphere: Theory, Experiments, and Applications (Cambridge University Press, 2014).
5. Holmes, C. D. et al. The role of clouds in the tropospheric NOx/NOy cycle. J. Geophys. Res. D: Atmos. 120, 4345–4372 (2015).
6. Davis, J., Bhave, P. & Foley, K. Parameterization of N2O5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate. Atmos. Chem. Phys. 8, 5295–5311 (2008).
7. Davis, J., Bhave, P. & Foley, K. Parameterization of N2O5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate. Atmos. Chem. Phys. 8, 5295–5311 (2008).
8. Thornton, J. A. & Abbatt, J. P. N2O5 reaction on smicron sea salt aerosol: Kinetics, products, and the effect of surface active organic species. J. Phys. Chem. A 109, 10094–10102 (2005).
9. Cheng, W. L. et al. Heterogeneous atmospheric chemistry, ambient measurements, and model calculations of N2O5: A review. Aerosol. Sci. Technol. 45, 665–695 (2011).
10. McDuffie, E. E. et al. Heterogeneous N2O5 uptake during winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current parameterizations. J. Geophys. Res. D: Atmos. 123, 4345–4372 (2018).
11. Karinova, N. V. et al. S2N2 reactions of N2O5 with ions in water: Microscopic mechanisms, intermediates, and products. J. Phys. Chem. A 124, 711–720 (2019).
Moeburg, D. R., Sharp, P. J., & Paesani, F. Molecular-level interpretation of vibrational spectra of ordered ice phases. *J. Phys. Chem. B* 122, 10572–10581 (2018).

Gaiduk, A. P., Pham, T. A., Govoni, M., Paesani, F., & Galli, G. Electron affinity of water. *Nat. Commun.* 9, 2478 (2018).

Sun, Z. et al. Electron-hole theory of the effect of quantum nuclei on the X-ray absorption spectrum of liquid water. *Phys. Rev. Lett.* 121, 137401 (2018).

Moberg, D. R. et al. The end of ice I. *Proc. Natl Acad. Sci. USA* 116, 24413–24419 (2019).

Cruzeiro, V. W. D., Wildman, A., Li, X. & Paesani, F. Relationship between hydrogen-bonding motifs and the 1b1 splitting in the X-ray emission spectrum of liquid water. *J. Phys. Chem. B* 122, 3996–4002 (2018).

Muniz, M. C. et al. Vapor-liquid equilibrium of water with the MB-pol many-body potential. *J. Chem. Phys.* 154, 211103 (2021).

Paesani, F., Bajaj, P. & Riera, M. Chemical accuracy in modeling halide ion hydration from many-body representations. *Adv. Phys.: X* 4, 1631212 (2019).

Riera, M., Mardiriossian, N., Bajaj, P., Götz, A. W. & Paesani, F. Toward chemical accuracy in the description of ion–water interactions through many-body representations. alkali–water dimer potential energy surfaces. *J. Chem. Phys.* 147, 161151 (2017).

Bajaj, P., Götz, A. W. & Paesani, F. Toward chemical accuracy in the description of ion-water interactions through many-body representations. I. Halide-water dimer potential energy surfaces. *J. Chem. Theory Comput.* 12, 2698–2705 (2016).

Riera, M., Yeh, E. P. & Paesani, F. Data-driven many-body models for molecular fluids: CO2/H2O mixtures as a case study. *J. Chem. Theory Comput.* 16, 2246–2257 (2020).

Riera, M., Hirales, A., Ghosh, R. & Paesani, F. Data-driven many-body models with chemical accuracy for CH3/H2O mixtures. *J. Phys. Chem. B* 124, 11207–11221 (2020).

Bedeaux, D. & Weeks, J. D. Correlation functions in the capillary wave model of the liquid–vapor interface. *J. Chem. Phys.* 82, 972–979 (1985).

Li, W., Pak, C. Y. & Tse, Y.-L. S. Free energy study of H2O, N2O5, SO3 and O3 gas sorption by water droplets/slabs. *J. Chem. Phys.* 148, 164706 (2018).

Sander, R. Compilation of Henry’s law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.* 15, 4399–4981 (2015).

Möller, F., Zahn, M. & Wahn, A. Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols. *Phys. Chem. Chem. Phys.* 1, 5451–5457 (1999).

Yeh, I.-C. & Hummer, G. System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions. *J. Chem. Phys.* 108, 15873–15879 (2004).

Hummer, G. Position-dependent diffusion coefficients and free energies from Bayesian analysis of equilibrium and replica molecular dynamics simulations. *N. J. Phys.* 7, 34 (2005).

Varylli, P. & Chandler, D. Water evaporation: A transition path sampling study. *J. Phys. Chem. B* 117, 4149–4148 (2013).

Chandler, D. Statistical mechanics of isomerization dynamics in liquids and the transition state approximation. *J. Chem. Phys.* 68, 2959–2970 (1978).

Grznić, G., Bartels-Rausch, T., Türlir, A. & Ammann, M. Efficient bulk mass accommodation and dissociation of N2O5 in neutral aqueous aerosol. *Atmos. Chem. Phys.* 17, 6493–6502 (2017).

Zwan zig, R. Nonequilibrium Statistical Mechanics (Oxford University Press, 2001).

Schle, A. J. & Limmer, D. T. Rate constants in spatially inhomogeneous systems. *J. Chem. Phys.* 150, 191102 (2019).

Niblett, S. P. & Limmer, D. T. Ion dissociation dynamics in an aqueous premelting layer. *J. Phys. Chem. B* 125, 2174–2181 (2021).

Gaston, C. J. & Thornton, J. A. Reacto-diffusive length of N2O5 in aqueous sulfate- and chloride-containing aerosol particles. *J. Phys. Chem. A* 120, 1039–1045 (2016).

Cohen, A. J., Mori-Sánchez, P. & Yang, W. Challenges for density functional theory. *Chem. Rev.* 112, 289–320 (2012).

Mardiriossian, N. & Head-Gordon, M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Mol. Phys.* 115, 2315–2372 (2017).

Mandal, S., Deb Nath, J., Meyer, B. & Nair, N. N. Enhanced sampling and free energy calculations with hybrid functionals and plane waves for chemical reactions. *J. Chem. Phys.* 149, 144113 (2018).

Roberts, J. M. et al. Laboratory studies of products of N2O5 uptake on Cl−-containing substrates. *Geophys. Res. Lett.* 36, L28008 (2009).

Case, D. A. et al. AMBER 20 https://ambermd.org (2020).

Riera, M. & Paesani, F. MBP: A many-body energy and force calculator. http://paesani.group.ucsd.edu/software/mbx.html. Accessed August 10, 2021.

Frenkel, D. & Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications* 2nd edn (Elsevier, 2002).

Kästner, J. & Thiel, W. Bridging the gap between thermochemical integration and umbrella sampling provides a novel analysis method: “Umbrella Integration.” *J. Chem. Phys.* 123, 144104 (2005).

Cruzeiro, V. W. D., Galbi, M., Limmer, D. T. & Götz, A. W. Data from: Insights into the uptake of N2O5 by aqueous aerosol using chemically accurate many-body potentials. Center for aerosol impact on chemistry of the environment (CAICE), UC San Diego Library Digital Collections. https://doi.org/10.6075/J0FF3SHB (2021).

**Acknowledgements**

We thank T. Bertram, B. Gerber, G. Nathanson, and F. Paesani for stimulating discussions. This work was funded by the National Science Foundation through the National Science Foundation Center for Aerosol Impacts on Chemistry of the Environment (NSF-CAICE) under grant number CHE 1801971 (D.T.L., A.W.G.). This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the NSF under grant number ACI 1548562 (A.W.G., resources at the San Diego Supercomputer Center and the Texas Advanced Computing Center).

**Author contributions**

D.T.L. and A.W.G. conceptualized and designed the work. V.W.D.C. and A.W.G. prepared the simulation models with many-body potentials of coupled cluster accuracy. V.W.D.C. performed the molecular dynamics simulations (umbrella sampling, scattering at the water/vapor interface, and N2O5 in bulk water). D.T.L. developed the reaction-diffusion model and executed the corresponding simulations. V.W.D.C., M.G., D.T.L., and A.W.G. performed data analyses. D.T.L. drafted the manuscript with contributions from all authors. D.T.L. and A.W.G. acquired funding and supervised this research.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information** The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-28697-8.

**Correspondence** and requests for materials should be addressed to David T. Limmer or Andreas W. Götz.

**Peer review information** *Nature Communications* thanks Davide Donadio, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

**Reprints and permission information** is available at http://www.nature.com/reprints

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.